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Reactions with Co and with Small Organic Molecules**

M.M. Kollrack
(Ph.D. Thesis)

November 1990

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**The Surface Chemistry of Si(111) (7×7): Reactions with Co
and with Small Organic Molecules**

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Ph.D. Thesis

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098.

The Surface Chemistry of Si(111) (7×7): Reactions with
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The reactions of Si(111) (7×7) surfaces with Co, benzene, and various alkyl iodides were studied to gain insights into the surface chemistry of this important semiconductor. The reactions of Co with Si(111) produced epitaxial $\text{CoSi}_2(111)$ films, a promising metallization material for Si semiconductor devices. The adsorption of benzene on $\text{CoSi}_2(111)$ was used to characterize this surface and compare its surface chemistry to that of Si(111). The thermal decompositions of alkyl iodides on Si(111) were studied to investigate the desorption mechanisms of alkyl groups. The intact desorption of alkyl groups is of critical importance in organometallic vapor deposition processes.

CoSi, and CoSi₂). The modification of the initial Co - Si interface with oxygen and nitrogen retarded the diffusion of Co into the Si substrate. This explains reports of simultaneous Co₂Si and CoSi formation for reactions not taking place under the atomically clean conditions of ultra-high vacuum.

The surface of epitaxial CoSi₂(111) films was studied in reactions with oxygen and benzene. Oxidation of CoSi₂ resulted in the formation of a surface silicon oxide. Heating this surface resulted in the removal of this oxide and a possible restructuring of the silicide film. Temperature programmed desorption (TPD) was used to examine the π bonding of benzene to CoSi₂(111) surfaces. Comparison of the TPD results of benzene on CoSi₂(111) to benzene TPD results on Si(111) suggests that CoSi₂(111) terminates in a (111) layer of Si.

The thermal decompositions of iodoethane, 1-iodopropane, and 1-iodo-2-methylpropane on Si(111) were investigated. All alkyl iodides decomposed to produce alkene desorption by a β dehydrogenation mechanism. γ dehydrogenation of 1-iodopropane and 1-iodo-2-methylpropane resulted in the desorption of ethene and propene and in the deposition of carbon. The relative amounts of β and γ abstraction are a function of the initial surface carbon content, with high carbon coverages favoring γ H abstraction and further carbon deposition. The implications for vapor deposition processes using alkyl precursors on Si(111) are discussed.

To my parents, without whose love and support
I would never have gotten this far.

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1. INTRODUCTION

The reactions that take place on Si(111) surfaces, including reactions with thin Co films and with small organic molecules, are examined in this thesis. The experiments were all performed in ultra-high vacuum to permit the preparation and characterization of surfaces and interfaces on the atomic scale. The reactions of Co films with Si(111) substrates at higher temperatures were investigated, including the effects of interfacial oxygen and nitrogen. The surface chemistry of the final product of the reaction between Co and a Si substrate is CoSi_2 , a material important to the semiconductor industry. The surface chemistry of CoSi_2 was studied using temperature programmed desorption. Finally, the thermal decomposition of alkyl iodides on Si(111) was explored, also using temperature programmed desorption. The insights gained from these thermal decomposition studies have important applications in the field of chemical vapor deposition using alkyl-substituted precursor molecules.

The surface of Si(111), like that of any solid, presents a unique environment for reactions to occur because of the special properties of atoms on the surface. Surface atoms differ from atoms in the bulk of a solid in that they have fewer neighboring atoms. For example, a surface atom on a (111) face of silicon has only three nearest neighbors, as opposed to a bulk atom which is bonded to four atoms. Surface atoms at step and kink sites have even fewer neighbors. The low coordination of surface atoms provides a

driving force for reactions on surfaces. The adsorption of molecules on surfaces and the surface reconstruction of many solids are two examples of lowering the energy of the surface by increasing the coordination of surface atoms.

The idea of a surface, as described above, is not limited to the surface of a solid that is exposed to a gas or vacuum. Perhaps a better term is "interface," since this term describes the surface of a solid exposed to a gas, liquid, or solid. The environment of an interfacial atom is still different from that of a bulk atom, though the number of nearest neighbors is not necessarily lower. Instead, the surface atom is unique because it is bound both to atoms of the same phase and to different atoms across the interface.

Reactions occurring on solid surfaces are of great importance in a variety of fields. One of the most prominent is the area of heterogeneous catalysis, where liquid or gas phase molecules adsorb and react on a catalyst surface. Catalysts increase reaction rates by lowering the activation energies necessary for reactions to proceed. Surface reactions are important to the field of corrosion, where it is desirable to slow or prevent reactions that alter the substrate material. Reactions that deposit atoms on surfaces are increasingly important alternatives to conventional deposition techniques such as evaporation and sputter deposition for the microelectronics industry. This industry is also interested in reactions that selectively remove (etch) atoms from surfaces, reactions which are necessary in the production of complex electronic devices.

The chemistry of semiconductor surfaces has received less attention in the past than the chemistry of transition metal surfaces because of the historical importance of transition metals in industrial catalysis.¹ Interest in semiconductor surface chemistry has increased recently, judging by the ever-growing number of articles appearing in the literature, and has been accompanied by the growing importance of this field. The very operation of semiconductor devices is based on the electrical properties of solid-solid interfaces. The continuing trend in microelectronics towards device miniaturization places increasing importance on the control and understanding of interfaces, since with the shrinking of device dimensions the interfacial region takes up a greater fraction of the volume of the junction.

The surfaces of semiconductors differ primarily from those of metals in the type of bonding that exists at the surface. Semiconductors are bound together by highly directional, covalent bonds. Semiconductors such as GaAs and Si have a tetrahedral arrangement of bonds around each atom. At the semiconductor surface, non-bonding electrons extend from the surface into space. In addition, the surfaces of most semiconductors are quite open due to the loose packing characteristic of covalently bound solids, increasing the lateral spacing between these localized dangling bonds.

Metals, in contrast, are held together by the non-directional metallic bonding of a sea of mobile electrons. Metal atoms are also packed much more densely than semiconductor atoms and are bound to as many as 12 nearest-neighbors, typically close-packed in face-centered cubic (fcc) or

hexagonal-close-packed (hcp) structures, or nearly so in body-centered-cubic (bcc) metals. The dense packing of atoms on metal surfaces, together with their non-directional bonding, distinguishes the surfaces of metals from those of semiconductors. The electron density at some fixed distance from a metal surface does not vary as strongly over the various surface sites as does the electron density over a covalent semiconductor.

The surface of a solid contains only a tiny fraction of the total number of atoms in the solid, typically on the order of 10^{-8} . To study surface atoms experimentally, it becomes necessary to selectively detect the contributions of these relatively few atoms over the far greater number of atoms in the bulk. One way of doing this is to maximize the number of surface atoms over the number of bulk atoms by increasing the surface area-to-volume ratio of the system.

Alternately, it is possible to selectively probe surface atoms using electron spectroscopies. The surface sensitivity of these techniques arises from the short mean free paths of electrons in solids, which range from about 5 Å and upward. This short mean free path means that the electrons originating from the bulk cannot escape the solid to be detected. This surface sensitivity of electron spectroscopies can be enhanced further by moving the detector to observe only electrons that emerge at small angles from the substrate. Electron spectroscopic techniques provided the surface sensitivity in the experiments described in this thesis.

Electron spectroscopies require that experiments be carried out in a vacuum to allow electrons to reach the detectors. The ultra-high vacuum (UHV) chamber used for experiments in this thesis (base pressure $<2 \times 10^{-9}$ Torr) also serves to keep surfaces free of adsorbate molecules present in the ambient, molecules which completely cover most surfaces that are exposed to atmosphere. Such compositional control is crucial to the preparation and characterization of surfaces on the atomic level.

Included in the silicon surface chemistry investigations of this thesis is a study of the reaction of cobalt films with a silicon substrate to form CoSi_2 . Cobalt is one of many transition metals that react with silicon to form metallic silicides. Much of the interest in metal-silicon reactions stems from the use of such transition metal silicides as electrical contacts in semiconductor devices.

The stability of many metallic silicides on silicon makes them excellent candidates for contacts. Most metals make poor choices for contacts because they react with silicon at room temperature and above, altering the composition of the interfacial region and changing the electronic properties of the junction. The high temperature processing of semiconductor devices contributes to further reaction of such metals with silicon. In contrast, many silicides are stable on silicon to temperatures approaching 1000°C , making them more reliable for electrical contacts.

The electrical properties of metal-semiconductor junctions are also degraded by any impurities present at the interface, which are especially likely for metal depositions performed under non-UHV conditions. In contrast, the

interfaces between many metallic silicides and silicon are free of impurities because the atoms of the overlying metal film diffuse past the impurities of the original metal-silicon interface to react with underlying silicon atoms. The resulting silicide is in intimate contact with the silicon substrate, and the contaminants remain on the surface of the silicide.

The importance of the interfacial region is not limited to the resulting electronic properties of these metal silicide systems. The interface also determines the solid state reactions that can occur between two phases, since any such reactions must take place at the interface. The bulk compositions of the overlayer and substrate must be considered, as well as the interfacial composition, which may include impurities not present in appreciable quantities in the bulk phases. Such impurities can make an interface unreactive, acting as a diffusion barrier to retard or even prevent a reaction that might otherwise proceed. Interfacial impurities might also change the products of the solid state reaction by changing the surface energies which control the nucleation of product phases.

In the study of the effects of interfacial impurities on the formation of CoSi_2 described in Chapter 3, the surface of the silicon substrate was modified before Co film deposition and subsequent annealing. Reactions of thin Co films with clean silicon surfaces were compared to those taking place across oxidized and nitrided interfaces by probing the evolution of the surface composition during the reaction. The surface crystallography of the final film was also characterized. The results obtained from these experiments show

that Co will diffuse past thin interfacial oxide and nitride layers to form CoSi_2 , but such a reaction is faster in the absence of interfacial impurities. The surface of the final CoSi_2 film is covered by a thin oxide or nitride film. The surface oxide sublimates near 700°C , possibly providing a new route to the removal of silicon from CoSi_2 surfaces.

Of the transition metal silicides, four have the additional advantage of forming epitaxial films on silicon wafers: Pd_2Si , PtSi , NiSi_2 , and CoSi_2 .² Epitaxial films are layers that grow as a single crystal over a single crystalline substrate, continuing the substrate structure into the overlayer. Epitaxial growth generally requires that the overlayer and substrate have similar crystal structures and a small difference in lattice parameters (usually less than 10%). CoSi_2 , which crystallizes in the cubic fluorite structure (CaF_2), has a lattice parameter 1.2% smaller than that of Si. The use of epitaxial silicides in electronic devices permits a reduction in the thickness of the metal-silicon contact and also in silicide film thickness, since the interface between an epitaxial overlayer and the substrate is abrupt and flat, unlike the interface of a polycrystalline overlayer. Epitaxial silicides, as single crystals, have the added advantage of lower resistivities compared to polycrystalline silicides, increasing the speed of the resulting semiconductor device.

Of the known epitaxial silicides, CoSi_2 grown on Si(111) has both the best epitaxial quality as well as the lowest resistivity.³ This makes CoSi_2 an attractive candidate in the construction of contacts and interconnects as devices become smaller and faster. In addition, CoSi_2 has the unique

property of being a template for the growth of an epitaxial layer of Si over $\text{CoSi}_2/\text{Si}(111)$.^{4,5} This opens up the possibility of forming novel 3-dimensional devices, such as the metal base transistor,^{6,7,8,9,10} in which the various components of the device are stacked vertically instead of next to each other on the chip surface. The formation of these devices depends on the ability to grow extremely thin (less than 100 Å) metallic films with atomically smooth interfaces. The advent of 3-dimensional devices promises to increase chip speed through a reduction in device size.

The formation of epitaxial CoSi_2 films on silicon substrates makes the study of single crystal surfaces possible without having to grow bulk silicide single crystals themselves. The experiments described in Chapter 4 explore the surface chemistry of $\text{CoSi}_2(111)$, focusing on the π - bonding of benzene adsorbed on the surface. The surface chemistry of CoSi_2 is compared to that of $\text{Si}(111)$ and to previous work on $\text{NiSi}_2(111)$.¹¹ The surface chemistry of CoSi_2 is of interest not only to understand the properties of this technologically important material, but also because the CoSi_2 surface is the site of the growth of epitaxial $\text{Si}(111)$ overlayers.

Finally, the reaction between metals and silicon can yield insight into the formation of rectifying contacts. For the silicide-silicon junction to be in equilibrium, the Fermi energies (the chemical potential of the electrons) of the two phases must be identical at the interface. This requires a rearrangement of charge for any materials with different Fermi energies. In a rectifying contact, this rearrangement of charge gives rise to a potential difference (the

Schottky barrier) at the interface which results in a junction whose resistivity depends on the direction of the applied voltage. The height of the Schottky barrier depends on more than the Fermi energies of the metal and semiconductor and is poorly understood. Many factors, which are all properties of the metal-semiconductor interface, influence the Schottky barrier height.¹² Silicides in general, and epitaxial silicides in particular, provide stable, well-characterized interfaces on silicon for studying the mechanisms of Schottky barrier height formation.

One area that has received little attention in the field of surface chemistry is the study of chemical vapor deposition (CVD) processes. In CVD processes, a volatile precursor molecule containing the atom to be deposited decomposes on a hot substrate, leaving behind the desired atom. This deposition is accompanied by the desorption of the remaining fragments of the original molecule.

Routes to the deposition of thin films are of importance to many fields. Coatings, for example, are used to modify the physical properties of surfaces such as hardness and friction. Coatings can improve chemical properties of surfaces, such as oxidation resistance or catalytic activity. Thin film depositions have many applications in the microelectronics industry, since devices are constructed by the selective deposition and etching of films.

Vapor deposition processes offer many advantages over other methods of film deposition such as evaporation and sputter deposition. These advantages include the high deposition rates possible and the low

temperatures needed to evaporate precursor molecules. By adjusting the rates of arrival of precursor molecules it is possible to grow compound films with excellent control over stoichiometry. In addition, at the relatively high pressures used (>20 mTorr), the short mean free path of the precursor molecules causes them to strike the substrate at all angles, ensuring good deposition coverage over any substrate contours. Such coverage is not possible with the line-of-sight deposition processes that occur in vacuum environments.

Vapor deposition processes are classified based on the type of precursor molecule used. The term chemical vapor deposition usually refers to processes using inorganic sources such as halides. The deposition of atoms from halide precursors often requires high substrate temperatures, which makes the deposition of metastable films more difficult. In addition, many CVD precursors are extremely toxic and corrosive.

A subgroup of CVD is organometallic chemical vapor deposition (OMCVD), which as the name implies, uses organometallic sources, though it includes the deposition of non-metallic atoms such as phosphorus. Organometallic sources are also used to grow epitaxial semiconductor films in a process known as organometallic vapor phase epitaxy (OMVPE).

The use of organometallic precursors (OMCVD, OMVPE) provides better control over the deposition process, since changing the organic ligands allows one to tailor the properties of the precursor to improve its volatility, lower the decomposition temperature, and decrease the amounts of impurities

incorporated into the deposited film. Many OMCVD precursors are much less toxic and corrosive than their CVD counterparts and often can be purified to a greater degree. Unlike CVD reactions, the decomposition of organometallic precursors is not reversible, creating the opportunity to form sharp (i.e. ungraded) interfaces. In addition, OMVPE has the economic advantage of being able to produce epitaxial films without the cost and complexity of UHV techniques.

Curiously, while the adsorption of organometallic precursor molecules has started to attract attention in the field of surface chemistry, the desorption mechanisms of the organic fragments has been largely ignored. This is an important omission, since no deposition can be successful without the complete desorption of these organic groups. To focus on the desorption of surface organic fragments produced by organometallic precursors, the thermal decomposition of alkyl groups adsorbed on Si(111) was investigated by detecting both the surface and gas-phase decomposition products. By studying adsorbed ethyl, n-propyl, and 2-methylpropyl groups, important insights into alkyl decomposition mechanisms on Si(111) were gained. The most surprising of these was the effect of previously adsorbed carbon on the decomposition products, a relationship that could only have been observed in a surface science study conducted in UHV.

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2. EXPERIMENTAL

2.1. INTRODUCTION

The study of single crystal surfaces requires the preparation and characterization of atomically clean and ordered surfaces. This necessitates the removal of any gaseous species that might react with these surfaces, either through adsorption or compound formation. While in some cases an inert gas atmosphere may be acceptable, the experiments described in this thesis were performed under vacuum. In an evacuated environment it is also possible to use electron spectroscopies to probe the composition and structure of the surface and to detect the desorption of molecules.

In order for electrons or desorbing molecules originating at the sample surface to be detected, their mean free paths (λ) must be longer than the dimensions of the vacuum chamber, which were on the order of 10 cm. A pressure of 1×10^{-4} Torr will ensure that electrons and desorbing molecules will have a mean free path greater than 30 cm and thus have a >99% probability of travelling from the sample surface to the appropriate detector without undergoing any gas-phase collisions.

Temperature programmed desorption (TPD) experiments impose far stricter requirements on the necessary vacuum, since it must be possible to detect the desorption of less than one layer of adsorbed molecules (one monolayer, or ML) over the residual background. For a 0.5 cm^2 surface of

Si(111), this involves the detection of fewer than 3.9×10^{14} molecules, and in practice requires a vacuum in the 10^{-9} to 10^{-10} Torr range.

Finally, the pressure must be low enough so that the sample surface is not contaminated by the adsorption of molecules from the vacuum environment. From the kinetic theory of gases,¹ the number of molecular collisions against a wall per unit time and area is given by $(n/V)(c/4)$, where (n/V) is the number density of molecules and c is the root mean square speed (rms) of these molecules. If one assumes that every molecule that strikes the surface becomes adsorbed and let $c = 5 \times 10^4$ cm/s, then at a pressure of 2.5×10^{-6} Torr a surface will be covered by one ML of molecules in one second. At 1×10^{-10} Torr, it would take almost 7 hours to completely cover this surface. The Si(111) and CoSi₂(111) surfaces studied have the added advantage of being fairly unreactive, so that these surfaces would stay clean for days and certainly much longer than the time necessary to perform experiments.

2.2. ULTRA-HIGH VACUUM CHAMBER AND EQUIPMENT

The vacuum environment was provided by a 50 liter non-magnetic stainless steel Varian ultra-high vacuum chamber, equipped with ports for viewing the sample and for the instrumentation used by surface chemistry. A schematic top view of the chamber is shown in Figure 2.1. A non-magnetic chamber is necessary because it does not affect the electron beams used to

characterize surfaces.

The ultra-high vacuum was achieved by first rough-pumping the system using two Varian sorption pumps in sequence. Sorption pumps work by removing molecules from the chamber by adsorption on a high surface area molecular sieve that has been cooled to liquid nitrogen temperature (-196°C). The first pump was only used to reduce the pressure in the chamber to about 1 Torr and then shut off, though the pump was still far from full capacity. The second sorption pump then lowered the pressure to the 10^{-4} to 10^{-5} Torr range after 5-15 minutes. Since sorption pumps are unable to remove molecules that do not adsorb on the molecular sieve at -196°C , the composition of the gas remaining in the chamber is primarily He and Ne. However, if the first sorption pump is shut off before saturation, these unreactive molecules are swept out of the chamber along with reactive molecules, thus increasing the overall pumping capacity of the sorption pumps. The sorption pumps were heated periodically between uses to improve pumping capacity by driving off any remaining adsorbed gases.

The rest of the pumping was performed by six 220 liter/s Varian Triode Vaclon pumps. The ion pumps were separated from the chamber by an isolation valve, which was opened slowly to keep the pressure near the ion pumps below $\sim 5 \times 10^{-4}$ Torr. Achieving the low 10^{-10} Torr range necessary for these surface science studies required baking the vacuum system at 250°C overnight to drive adsorbed water from the walls of the chamber so that it could be pumped away. The base pressure reached by this system

was always below 2×10^{-10} Torr.

The chamber was also equipped with a titanium sublimation pump which was particularly effective in removing hydrogen and water, gases that are difficult to remove with ion pumps. Ti sublimation pumping consisted of resistively heating a 75 mil Ti filament to deposit a fresh Ti film on the surface of a surrounding cylindrical shield. Molecules were then removed from the chamber by adsorption on this fresh Ti film. The Ti sublimation pumps were always used when evacuating the system after exposure to the atmosphere. At pressures in the 10^{-8} to 10^{-9} Torr range, the evaporation of Ti resulted in an immediate reduction in the pressure of the chamber. The evaporation was continued until the heat produced by this evaporation eventually caused the chamber pressure to increase. When used to obtain a low H_2 background pressure once the base pressure was in the 10^{-9} to 10^{-10} range, Ti was sublimed on the surrounding shield for 2 to 3 minutes every half hour. Maintenance of the base pressure required only occasional usage of the Ti sublimation pump.

A nude ionization gauge measured the pressure in the chamber once the ion pumps were started. In this gauge, electrons created at a filament were confined in space by a grid held at a positive potential. The molecules ionized in this region by the electrons were accelerated towards a negatively charged collector wire, and the neutralization current measured. This neutralization current is proportional to the number of molecules in the ionization region and hence to the pressure. No corrections to the pressure

measurements were made based on the sensitivity of the ionization gauge to various molecules.

A bakeable gas manifold was connected to the system to permit the introduction of gas molecules to the vacuum chamber. This manifold could be rough-pumped by the same two sorption pumps used for the main chamber, and then pumped by its own Varian Triode VacIon 20 litre/s ion pump to achieve pressures of about 1×10^{-8} Torr. Two isolable tubes connected this manifold to the chamber, through sapphire leak valves that could be used to introduce gases into the chamber at pressures from just above the base pressure to pressures above 10^{-4} Torr. Two tubes extended into the chamber from the leak valves and were used to direct gases at the sample surface from a distance of only 1 mm. This arrangement increased the local pressure near the sample surface, thereby reducing the exposure of the adsorbate to the rest of the chamber and permitting faster recovery of the base pressure.

The Si sample was attached to a two-piece block of oxygen-free copper mounted on the end of a manipulator. The two halves of the Cu block were electrically isolated from each other but connected to electrical feedthroughs on the manipulator flange. This allowed resistive heating by passing current through the sample. Cooling was accomplished using a cold finger mounted next to the manipulator on the same flange. The cold finger was connected to the Cu block via copper braids. By flowing liquified air through the cold finger, Si temperatures below -50°C were routinely reached.

The manipulator extended downward into the chamber and could be rotated around a vertical axis. The end of the manipulator was offset by 2.5 inches, which increased the diameter and the number of ports of the chamber while still permitting close approach of the crystal to the various ports. With this manipulator the sample assembly could be rotated around a horizontal axis from vertical to downward-facing, though mounting considerations limited the range of this rotation to about 30°. The sample was grounded on the atmospheric side of the manipulator flange to permit either grounding the sample or detecting the current between the sample and ground.

The mounting of silicon presents several difficulties for UHV silicon surface studies. Silicon, unlike most metals, cannot be spot-welded to metal support wires, which is the most common method of sample mounting. This presents problems not only in sample heating, which is usually done resistively by passing current through the sample, but especially in temperature measurement using a thermocouple junction, since spot-welding thermocouple wires to the sample is not possible. In addition, the silicon sample must still be in electrical contact with the mounting assembly because the use of electron spectroscopies for sample characterization requires grounding the sample to avoid sample charging.

To surmount these difficulties, two silicon mounting methods were employed. The first method² was to drill a 0.015 inch hole through the silicon chip near one edge. The thermocouple wires (Chromel-Alumel type K) were then drawn through this hole and spot-welded together. As these

thermocouple wires were each 0.005 in. in diameter, the resulting weld was approximately the same size as the hole in the silicon chip. The ends of the wires were then clipped and the weld was wedged in the 0.015 in. hole. The short lengths of wire remaining on the other side of the spot-weld were spread apart to help prevent the thermocouple junction from slipping out of the hole in the silicon. The silicon was then mounted on 3 mil tantalum foil having the same shape as the silicon chip, and held in place by small tabs extending from the Ta foil. Both ends of the Ta foil were spot-welded to 30 mil Ta wires, which were attached to the copper mounting block of the manipulator. Heating the silicon was done by passing current through this Ta foil, with the result that the foil became much hotter than the silicon. At the SiO₂ sublimation temperature (850-900°C), a thermocouple spot-welded to the Ta foil revealed it to be over 300°C hotter than the silicon.

This mounting system was quite robust and usually gave reliable temperature readings, judging by the temperature necessary to desorb H₂ (580°C for low coverages) and SiO₂, as well as by comparisons to identical TPD experiments using the other silicon mounting technique (described below). The big disadvantage of this method was the tendency of the thermocouple junction to slip out of the hole in the silicon at high temperatures. This probably resulted from the softening of the ends of the thermocouple wires at elevated temperatures to the point where any stress in the thermocouple wires leading to the silicon was sufficient to pull the entire junction out of the hole in the silicon.

The second technique of silicon mounting was a modification of the method of Bozack et. al.³, in which silicon was glued to a support using Aremco Ultra-temp 516 high temperature ceramic adhesive. The same Ta support that was used in the aforementioned "thermocouple in the hole" method was also used here, although the tabs in the Ta foil were not always present. The backside of the silicon and the front of the Ta foil were first each covered with a thin layer of adhesive. At this point the thermocouple (again 0.005 mil Chromel-Alumel type K) spot-weld was held in the thin layer of adhesive on the back side of the silicon for about 5-10 min. until the adhesive had set. This was done to ensure close proximity of the thermocouple junction to the silicon for the most accurate temperature measurement. Roughening both surfaces with emery paper helped the adhesive bind to each surface, though this was not always done to the back of the silicon chip. These adhesive layers were allowed to dry in air for 4 hours before adding more adhesive to the Ta side and joining the two pieces. In this step the silicon was pressed to the Ta mounting assembly for about 15 minutes using a cotton swab and allowed to dry for an additional 4 hours. Care was taken not to release the pressure on the Si to avoid drawing air into the adhesive. The manipulator was then placed back in the vacuum chamber and the system evacuated using first the sorption and then the ion pumps. Due to the release of moisture from the adhesive, the system was pumped on by the ion pumps overnight before proceeding. The adhesive was dried by slowly heating the sample assembly to 90°C and keeping it

there for 160 minutes. Curing the adhesive was accomplished during the overnight bakeout of the chamber, which lasted 16 hours at a temperature of 250°C. Heating the sample assembly to 300°C served to fire the adhesive. Finally, the temperature was raised to 800°C over one hour to drive off any molecules still adsorbed on the adhesive.

The first annealing of the sample above the final curing temperature was accompanied by substantial outgassing, but once the sample had been cycled to its maximum temperature (900°C to sublime SiO), no further outgassing occurred. In fact, this adhesive was UHV-compatible to 1200°C, which was near the end of the thermocouple scale and close to the melting point of silicon (1412°C). The excellent thermal contact between the silicon and the supporting Ta foil actually reduced the amount of desorption from the mounting assembly compared to the first mounting scheme because much less heating current and consequently lower Ta temperatures were required to reach a given silicon temperature. The disadvantages of this mounting scheme were the greater effort and time required to mount the Si and the fragility of the adhesive junction to physical shocks. With proper care, however, a sample mounted in this manner gave many months of reliable temperature measurements before the gradual failure of the adhesive. This technique was used for the majority of the experiments described in this thesis. To ensure the accuracy and reproducibility of the thermocouple temperature measurement, the desorption temperature of H₂ and the temperature of sublimation of SiO were again used as an internal temperature

standards.

Cobalt was deposited onto silicon substrates using a 2 kW electron beam evaporator made by VG Instruments. The evaporator was located under the manipulator in the lower half of the chamber. The material to be evaporated (in this case Co) was placed in a Nb crucible which was mounted on a water-cooled hearth. A cylindrical stainless steel shield above the crucible prevented the deposition of Co throughout the chamber.

The electron source consisted of two semi-circular filaments surrounding the crucible. These filaments were negatively biased to accelerate the electrons at a grounded target. Before Co deposition, the shield was heated for one hour by electron bombardment by biasing the crucible at the filament voltage and grounding the shield. This was done to reduce outgassing from the shield during the evaporation. The Co was heated by floating the shield and grounding the crucible. In order to remove any adsorbed or dissolved impurities in the Co, the crucible was brought to a temperature at which the evaporation rate was still negligible (one Å every few min.). Outgassing was always performed with the Si facing away from the evaporator. For Co evaporation, the Si sample was rotated above the source and rotated downward to face the rising Co flux. During the actual Co deposition, the background pressure varied from the low 10^{-8} to 10^{-9} Torr range.

Deposition was monitored with a quartz microbalance above the evaporator. The accuracy of this balance was questionable for the lowest

thicknesses used here (as little as 10 Å). In addition, the reciprocal density of Co used ($0.112 \text{ cm}^3/\text{g}$) was not a good choice for low coverages of Co on Si(111), where the Si substrate determines the Co density.

2.3. REAGENTS

Si(111) (p-type, 5-50 ohm-cm), purchased from the Microlab of the CS/EE Department of the University of California, Berkeley, was used in this study. Samples were obtained by breaking 2 in. or 3 in. wafers and collecting pieces of appropriate size and shape for mounting. Most often this was a parallelogram with sides between 5 and 8 mm long. The Si was first degreased with ethanol and then mounted on Ta foil using one of the two methods described above.

Small pieces of Co wire (Aldrich, 1.0 mm diameter, 99.995% (Gold Label)) were used as the Co source. Benzene (99%), used in adsorption experiments on Si and CoSi_2 , was purchased from Fisher. Iodoethane (99%), 1-iodopropane (99%) and 1-iodo-2-methylpropane (97%) were obtained from Aldrich. Oxygen (99.6%), nitrogen (99.9%), and argon (99.998%) (all from Matheson) were used without further purification.

All adsorbates were put through at least 3 freeze-pump-thaw cycles on a glass vacuum line to remove dissolved gases. The gas manifold and leak line were then flushed at least twice with adsorbate vapor before introduction of the adsorbate into the UHV chamber. No impurities in the adsorbates

were detected by mass spectroscopy.

2.4. SPUTTER CLEANING

While the surfaces of Si and CoSi_2 were fairly unreactive towards the adsorption of residual gases in the vacuum chamber, periodic cleaning of these surfaces was still necessary. In addition, adsorbate decomposition during TPD experiments contributed to the accumulation of surface contaminants. The primary contaminant in these experiments was carbon, though oxygen, and nitrogen were occasionally present as well. The method most often used to clean the sample surfaces was argon ion sputtering. In this technique, both substrate and adsorbate atoms were removed by bombarding the surface with high energy Ar^+ ions.

Before sputtering, the ion pumps were isolated from the rest of the chamber, and argon admitted into the chamber through one of the dosing tubes. The Ar was pumped away by a turbomolecular pump, with the leak rate of Ar into the chamber adjusted to maintain a constant pressure of Ar. The turbomolecular pump removed any gases evolved by sputtering and helped the chamber recover its base pressure faster, as the ion pumps are inefficient in pumping noble gases. The Ar^+ beam struck the surface at an angle of 11.5° from parallel with an energy of 1600 eV. An Ar pressure of $\sim 7 \times 10^{-5}$ Torr was found to maximize the crystal to ground current at $\sim 10 \mu\text{A}$. This current corresponds to a sputter rate of 3.6 ML/min under the

assumption that each Ar^+ removes one surface atom. Sputter times used ranged from 12 to 30 minutes.

Sputtering at such high energies damages the Si surface and implants Ar into the near surface region. In addition, oxygen was often detected on the sample surface after sputtering, even when there was no oxygen present initially. This surface oxygen was attributed to the acceleration of oxygen-containing molecules at the sample surface (by the sputter gun and by collisions with Ar^+), and by adsorption of such molecules on the roughened surface created by sputtering. Roughened surfaces are more reactive to adsorption because of the decreased coordination of the surface atoms.⁴

Flushing the chamber by first admitting 2×10^{-4} Torr of Ar and then pumping to 3×10^{-7} Torr with the turbomolecular pump before refilling with Ar and sputtering improved the cleanliness of the resulting surface. Most likely argon atoms colliding with the walls of the chamber knock adsorbed molecules into the gas phase, where they are pumped away. This results in a purer Ar environment for sputtering.

The surface order was restored by annealing the Si to 900°C for about 10 minutes. This anneal also served to desorb Ar and to remove any oxygen. CoSi_2 surfaces were not cleaned by sputtering. Rather, once these surfaces accumulated carbon or other impurities, the whole silicide film was sputtered away and a new silicide film prepared. This avoids the difficulties of attempting to sputter impurities from a film only 40-100 Å thick.

2.5. AUGER ELECTRON SPECTROSCOPY

The compositions of the surfaces studied were determined using Auger electron spectroscopy (AES). In the Auger process, a sample is bombarded by photons or electrons with energies in the keV range to remove a core electron. The ionized atom relaxes when a valence electron drops down to fill this core vacancy. The energy released by this electronic transition can be removed by a photon or, in the Auger process, by the ejection of a valence electron (the Auger electron). The relative probability that Auger emission will occur depends on the energy of the ionization source and on the type of atom involved. All elements can undergo the Auger process with the exception of H and He, which have too few electrons.

The Auger emission process is shown schematically in Figure 2.2. The nomenclature used for AES describes the energy levels involved in the Auger process. For example, the term Si (MNN) refers to the Auger electron originating in the N shell which was ejected by the energy released when another N electron filled a vacancy in the M level.

The Auger electron has a kinetic energy equal to the energy released by the filling of the core hole by the valence electron minus the binding energy of the ejected (Auger) electron.

$$KE \sim BE(\text{core}) - BE(\text{relaxing electron}) - BE(\text{Auger electron}) \quad (1)$$

Since the Auger electron's energy depends on the electronic energy levels of the ionized atom, it is unique and can be used to identify this atom. In addition, the kinetic energy of the Auger electron is affected by changes in the electronic energy levels of the source atom, and so Auger electron spectroscopy also provides information about the chemical state of the atom.

The Auger electrons most often used for surface characterization have energies between 50 and 550 eV. The mean free path (λ) of such electrons in solids is only about 5 to 10 Å, so the Auger electrons that reach the detector must have come from the topmost layers of the sample. Auger electrons created further than 3λ from the surface have less than a 1% chance of escaping the sample and being detected, making analysis using Auger electrons in this energy range a surface sensitive technique. Surface sensitivity is an extremely important advantage of electron spectroscopies, since the number of atoms in the bulk is many orders of magnitude greater than the number of surface atoms in these single crystal systems.

An electron beam is the simplest excitation source for the production of Auger electrons. X-rays also provide the core ionization required by AES, but these more complex sources are normally used only in conjunction with photoelectron spectroscopic studies. In the experiments described in this thesis, a 2 keV electron beam was used as the Auger excitation source. To improve the yield of Auger electrons, the incident electron beam struck the sample at a grazing angle. This favored the production of Auger electrons in the near surface region, from which they could escape the sample and be

detected.

Detection of Auger electrons was accomplished using both a 4-grid retarding field analyzer (RFA) and a single pass cylindrical mirror analyzer (CMA). The RFA was used for the experiments described in Chapters 3 and 4, after which all Auger spectra were collected with the CMA. The grazing angle of the incident electron beam was determined by the geometry of the available ports on the chamber. The angle was 11.5° with the RFA and 19.0° when using the CMA.

The RFA is a high pass energy analyzer and is shown in Figure 2.3. It consists of 4 hemispherical grids, the outer two of which are grounded. A potential is applied to the second and third grids, which is increased linearly over the energy range of the electrons to be detected. Any electrons with energy greater than this retarding potential pass through to the phosphor screen, where they are counted as current. The spectrum obtained (I vs. E) in this way is then differentiated to yield $N(E)$ vs. E , the energy distribution of Auger electrons. This is done experimentally by adding a low amplitude, high frequency sinusoidal (AC) rider to the voltage ramp of the middle grids, which enables the use of a lockin amplifier to differentiate the spectrum. In practice, the spectrum is usually differentiated a second time to give the typical first derivative ($dN(E)/dE$) spectrum, shown schematically in Figure 2.4.

The CMA is a bandpass energy analyzer that detects electrons leaving the surface at a fixed acceptance angle. The CMA (Figure 2.5) has a grounded inner cylinder and a negatively charged outer cylinder, the potential

of which is ramped linearly to detect Auger electrons over a desired energy range. Only electrons having energies $E \pm \Delta E$ reach the detector, where the signal is amplified by an electron multiplier. As in the case of RFA detection, a sinusoidal component is usually added to the applied voltage ramp so that the first derivative ($dN(E)/dE$) spectrum is obtained using lockin amplification.

The purpose of the phase sensitive detection of the lockin amplifier is to isolate the Auger signal from the background noise and from electrons not coming from the Auger process, as well as to differentiate the spectrum. In this process, however, valuable information about the chemical state of an atom can be lost.⁵

The evolution of the surface composition of the Co/Si(111) system as a function of temperature (Chapter 3) was studied with AES by measuring the intensities of the Co (53 eV) and Si (92 eV) Auger peaks in the first derivative ($dN(E)/dE$) mode. The similarity in energies and consequently mean free paths (λ) of these Auger electrons ensures that both processes originate in the same near surface region. The sample was heated from room temperature past the formation temperature of CoSi_2 at a rate of $12^\circ/\text{min}$. The aim of the incident electron beam was optimized several times to compensate for any changes in the crystal position caused by thermal expansion. The crystal faced the RFA, which detected electrons with energies between 30 and 100 eV. Scanning this energy range took about 30 seconds and was repeated continuously for the duration of the experiment. Scanning the whole Co (53 eV) and Si (92 eV) Auger transitions, while more-

time consuming than just measuring the peak to peak heights, has the important advantage of providing chemical information from the lineshape of Si.

2.6. LOW ENERGY ELECTRON DIFFRACTION

Structural information about the various surfaces studied was obtained by the diffraction of electrons off these surfaces in a technique known as low energy electron diffraction (LEED). LEED is the two-dimensional analogue of X-ray diffraction, which exploits the wave nature of electrons to give diffraction off a two-dimensional, periodically repeating surface lattice. The diffraction of electrons by solids was first predicted by de Broglie in 1924 and observed in 1927 by Davisson and Germer.

The de Broglie wavelength (λ) of an electron is given by

$$\lambda = h / p \quad (2)$$

$$= h/(2mE)^{1/2} \quad (3)$$

where h is Planck's constant, and p , m , and E are the momentum, mass, and energy of the electron, respectively. Electrons are diffracted off an ordered surface according to the Bragg equation

$$n \lambda = d \sin(\theta) \quad (4)$$

where n is an integer, d is the distance between rows of surface atoms, and θ is the scattering angle.

The diffraction patterns obtained by LEED give information about the periodicity of the surface. This includes information about the reconstruction of the surface, whether it involves a simple relaxation in the topmost layers or a new surface periodicity, and also information about the ordering of adsorbate molecules. The degree of surface order was determined from the brightness and sharpness of the diffraction spots and the background intensity.

The apparatus for observing LEED patterns uses the same 4-grid analyzer used by the RFA for AES. For LEED, the inner two grids were held at negative potential slightly lower than the beam voltage to reject any electrons not diffracted elastically. The first and fourth grids were grounded to reduce any stray fields existing in this region. Any electrons passing through all four grids were then post-accelerated at a phosphor screen, where the diffraction pattern was observed as bright spots (Figure 2.6). The source of electrons was an electron gun mounted in the center of the grids, which struck the sample at perpendicular incidence. This gun produced a monoenergetic electron beam whose energy could be varied between 40 and 220 eV.

2.7. TEMPERATURE PROGRAMMED DESORPTION

The adsorption of molecules on surfaces is classified based on the type of bonding as either physical adsorption or chemisorption (chemical adsorption). In physical adsorption, molecules are bound to a surface by van der Waals forces (induced dipole); chemisorption is defined as adsorption involving the transfer of electrons and is consequently a stronger interaction than physical adsorption. The distinction between physical adsorption and chemisorption is not so clear cut in practice, however, and a binding energy of 10 kcal/mol is often taken as the boundary dividing the two.

In this thesis, information about the strength of the adsorbate-surface bond (i.e. adsorption energy) was obtained by heating the adsorbate-covered crystal and measuring the rate of desorption as a function of temperature in a technique known as temperature programmed desorption (TPD). In TPD experiments, the rate of desorption increases with temperature until a maximum is reached, when the depletion of the adsorbate concentration causes the rate to decrease. The shape of the desorption peak and the temperature at which the maximum desorption rate occurs were used to calculate values for the various parameters of the desorption process. The most important of these are the activation energy of desorption and the reaction order. The heat of adsorption is equal in magnitude (though opposite in sign) to the activation energy of desorption only when desorption is an unactivated process. In all other cases the activation energy of

desorption is the upper limit of the heat of desorption.

In TPD experiments, a surface was exposed to adsorbate molecules and heated until desorption was complete. TPD experiments were performed in an UHV chamber, which provided the facilities for the preparation and characterization of sample surfaces. Before exposing a surface to adsorbate molecules, the surface was checked for cleanliness by Auger electron spectroscopy (AES), and by low energy electron diffraction (LEED) to verify the order and characteristic reconstruction of the clean sample surface. Hydrogen, produced by the filaments of these electron guns and from exposure to the ionization gauge, was removed from the sample surface before any experiments by heating the sample to 700°C.

Prior to any gas adsorption on the sample surface, the sample was cooled to -50°C. The manipulator was then rotated so that the sample faced one of the dosing tubes at a distance of about 1 mm. The adsorbate was introduced into the chamber by opening a leak valve. The exposure of the surface to the adsorbate gas was determined by the pressure, which was held constant during a given experiment, and by the duration of the exposure. Unless noted, no calibration of the adsorbate exposure was done. The ionization filaments of the mass spectrometer affected the pressure measurement of the ionization gauge, and so these filaments were turned off before admitting any adsorbate into the chamber. After the dose, the mass spectrometer was turned on again, and the remaining gas was pumped away for at least three minutes to reach the base pressure of $<2 \times 10^{-10}$ Torr. If it

was not done already, the mass spectrometer was centered on the mass spectral peak of interest.

The sample was rotated until it faced the mass spectrometer, and heated by passing current through the Ta foil holding the Si crystal. The heating rate for all TPD experiments was close to 30°C, though it varied slightly depending on the Si mounting arrangement and on the maximum temperature reached during heating. The heating rate was always linear in the region of interest (100-600°C). Desorbing molecules entered the mass spectrometer and were recorded as a function of temperature. The mass spectrometer was equipped with two shields, each with a hole in the middle, to prevent molecules not originating at the sample surface from reaching the mass spectrometer.

A dedicated microcomputer (Uthe Programmable Peak Selector, PPSD) was used when more than one mass spectral fragment was to be detected during a single desorption experiment. This computer controlled the quadrupole of the mass spectrometer and allowed up to 10 mass fragments to be monitored simultaneously. The peak selector scanned through each peak in 10 steps, spending 1 ms at each step to find the peak maximum. This was followed by a delay of 5 to 15 ms before scanning through the next peak. The number of data points taken during a single experiment was fixed, so that monitoring an increased number of mass spectral fragments reduced the number of data points recorded for each fragment. Following more than 5 fragments simultaneously resulted in a trace that was unacceptably noisy

due to the lack of data points and was not done. The data were recorded as a function of time, not temperature, by the computer and converted to temperature by comparison to real-time TPD curves or by using the known heating rate. After the TPD flash the sample was cooled again, and the surface composition measured by AES to check for adsorbate decomposition. Before exposing the surface to the adsorbate for another experiment, the sample was heated to remove hydrogen and cooled again.

Nearly all adsorbates studied had initial desorption peaks occurring at the start of sample heating. These peaks were due to the desorption of multilayers, which are bound by physical adsorption, not chemisorption. In addition, an increase in the intensity of some mass spectral fragments near the end of the heating ramp was observed. As the crystal was heated, the manipulator and mounting assembly were slowly heated as well, resulting in desorption from these surfaces.

The TPD results presented in this thesis were analyzed using the method of Redhead.⁶ In this simple analysis, the rate of desorption as a function of time is given by

$$R_{\text{des}}(t) = -dN/dt = \nu N^2 e^{-E_a/RT} \quad (5)$$

where

ν = pre-exponential frequency factor

N = surface coverage

z = reaction order

R = gas constant

E_a = energy of activation of desorption.

Using a linear heating rate β such that

$$T = T_0 + \beta t \quad (6)$$

the activation energy of desorption can be found by differentiating. For first order desorption processes ($z = 1$), the resulting equation is

$$E_a/RT_p^2 = (v/\beta) e^{-E_a/RT_p} \quad (7)$$

or

$$E_a = RT_p \ln(vRT_p^2/E_a\beta). \quad (8)$$

The desorptions studied here were all first order with the exception of the second order desorption of H_2 , which was observed from the decomposition of iodides. H_2 desorption that resulted from the adsorption of H atoms produced from the background H_2 by hot filaments in the vacuum chamber was also detected. The activation energy of desorption for a second order process ($z = 2$) is found in terms of the initial surface coverage N_0 by

differentiating equation (5):

$$E_a/RT_p^2 = (N_0^{1/2}/\beta) e^{-(E_a/RT_p)} \quad (9)$$

Equation (9) contains a coverage dependent term missing for first order desorption (equation (7)). This term arises because two H atoms must combine before H₂ desorption can occur. The peak desorption temperature of this second order process is coverage dependent. In order to use the peak desorption temperature of H₂ from Si(111) as an internal temperature reference, a constant, low coverage of atomic H from the background was used. This constant hydrogen coverage was verified by measuring the area under the desorption peak, which remained constant.

The coverage independence of the desorption temperature in first order processes ignores adsorbate-adsorbate interactions, which are repulsive for adsorbates of a given species. This repulsion lowers both the desorption temperature and energy and may suggest a coverage dependent second order process. Neither the benzene desorption temperatures in Chapter 4 nor the alkene desorption temperatures in Chapter 5 displayed any coverage dependence.

One of the shortcomings of this simple approach is the need to assume a value for the pre-exponential frequency factor ν . This is not absolutely necessary, as ν and E_a can be determined independently by varying the heating rate β . In practice, however, it is not always possible to

vary β over a sufficient range to ensure accuracy. The possible heating rates for the experiments described in this thesis were limited to between 25 and 50°C/s, which did not permit an independent calculation of v . In such instances a value of 10^{13} s^{-1} for v is commonly used, as was done here for the benzene desorption experiments in Chapter 4. This value for v is derived from the desorption of a mobile atom in a one-dimensional potential; for immobile molecules a typical value of v is 10^{16} to 10^{17} s^{-1} . In Chapter 5 abnormally wide desorption peaks were observed. These wide desorption peaks were either combinations of thinner peaks or single peaks having a much lower pre-exponential factor. To calculate E_a for a single, wide peak, v was varied until the peak width calculated using the Redhead model matched the experimental desorption peak width. The analyses in this thesis do not take into account the possible coverage and temperature dependence of the pre-exponential factor⁷ nor the possibility of intermediate states in the desorption process.⁸

The quantization of TPD data was done by integrating the area under the desorption peak in most cases. Integration of overlapping peaks is more difficult since it requires information about each individual peak shape. In Chapter 5, overlapping peaks were observed for a single TPD trace from mass spectral fragments originating from different desorbing molecules. In this Chapter the desorption peak height was used as a measure of the amount of each desorbing species instead of the peak area. The justification for this was given by Redhead,⁶ who showed that the desorption rate at T_p is

proportional to the initial surface coverage N_0 for a first order desorption process. This is equivalent to saying the desorption peak height is proportional to the number of desorbing molecules, and hence to the area under the desorption peak.

This relationship between the desorption peak height and the initial surface coverage can be found by integrating equation (5) to find the surface coverage at T_p :

$$\ln(N_0/N_p) = (\nu R / E_a \beta) [T_p^2 e^{-E_a/RT_p} - T_0^2 e^{-E_a/RT_0}] \quad (10)$$

and when substituting from (3), above,

$$\begin{aligned} \ln(N_0/N_p) &= 1 - (T_0/T_p)^2 e^{-(E_a/RT_0 - E_a/RT_p)} \\ &\approx 1 \end{aligned} \quad (11)$$

or

$$N_p = N_0/e. \quad (12)$$

Substituting equation (12) into the original rate of desorption equation (5) gives

$$R_{des}(T_p) = \nu N_0 e^{-(E_a/RT + 1)}, \quad (13)$$

justifying the original assumption (used in Chapter 5) that the desorption peak height varies linearly with the initial surface coverage.

Information about the bonding of adsorbates that is not provided by TPD may be obtained from various electron spectroscopies. In x-ray photoelectron spectroscopy (XPS), monochromatic x-rays are used to remove core electrons, whose energies are measured. By subtracting the energies of the ejected electrons from the energy of the incident photon, the energy levels of core electrons are calculated. These core energy levels provide information about the oxidation state of the atom, that is, the amount charge transfer. Ultra-violet photoelectron spectroscopy (UPS) is a closely related technique that utilizes lower energy photons to eject valence electrons. The energy levels of these valence electrons yield information about the molecular orbitals of the adsorbate itself and of the adsorbate-surface complex.

Vibrational spectroscopy provides insights into the interactions involved in adsorption, both by probing the adsorbate-surface bond and by examining the changes in the vibrational spectrum of the adsorbate itself. Infra-red spectroscopy is sensitive to vibrations of suitable symmetry, but its application to adsorbates on single crystals is made difficult by the low probability of vibrational excitation by photons. This low cross-section requires a large surface area system to maximize the number of vibrations. Electrons have a much greater probability of exciting molecular vibrations and are better suited to single crystal studies. In high resolution electron energy loss spectroscopy

(HREELS), electrons strike a crystal and return to a detector with energies lower than the incident energy by an amount equal to the energy of the vibrational mode excited. HREELS requires a monoenergetic electron beam with energies in the meV range for good resolution.

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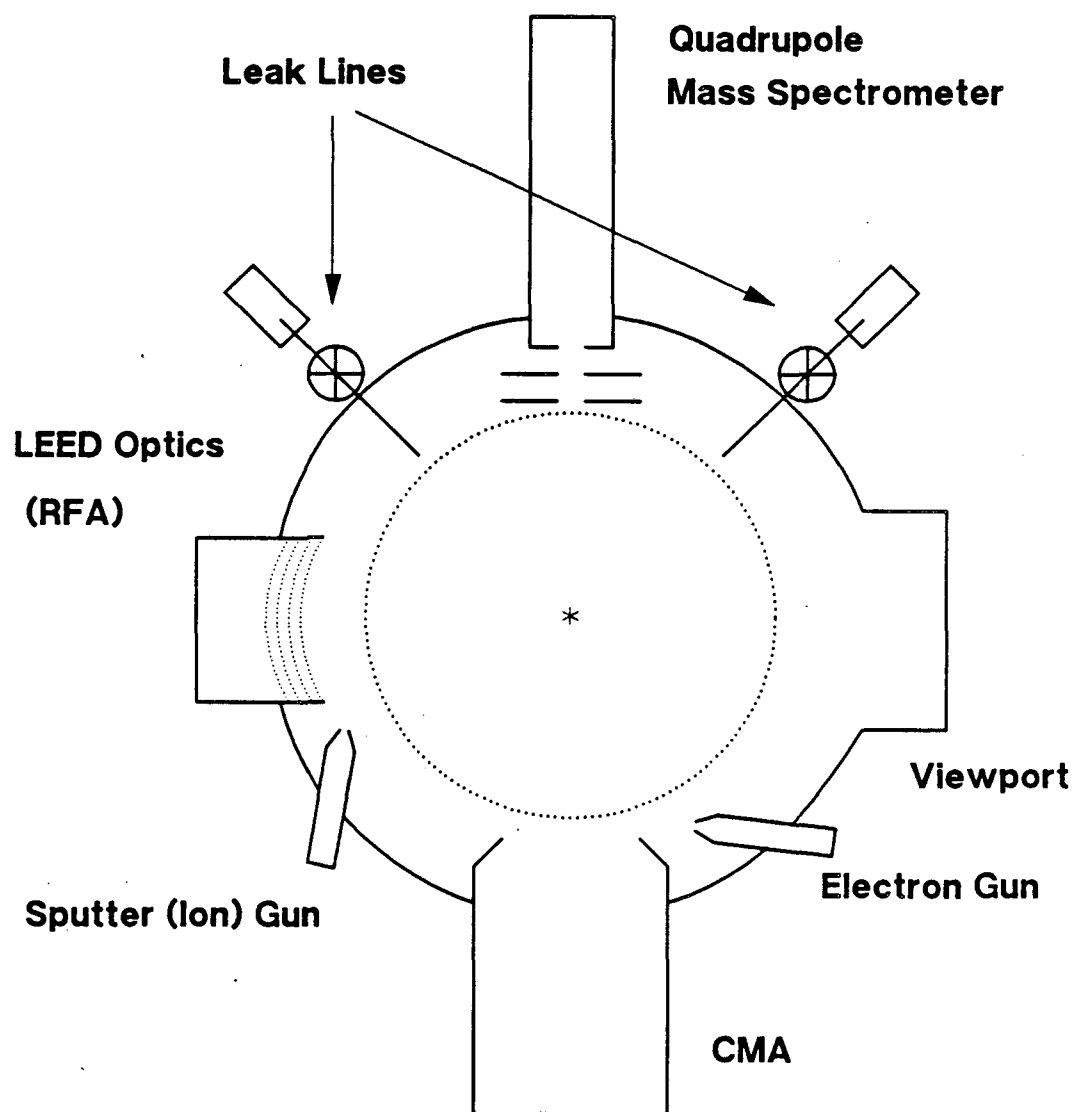


Figure 2.1. Top-view diagram of ultra-high vacuum chamber in which the experiments of this thesis were performed. Facilities for the preparation and characterization of Si surfaces are shown.

Auger Electron Emission

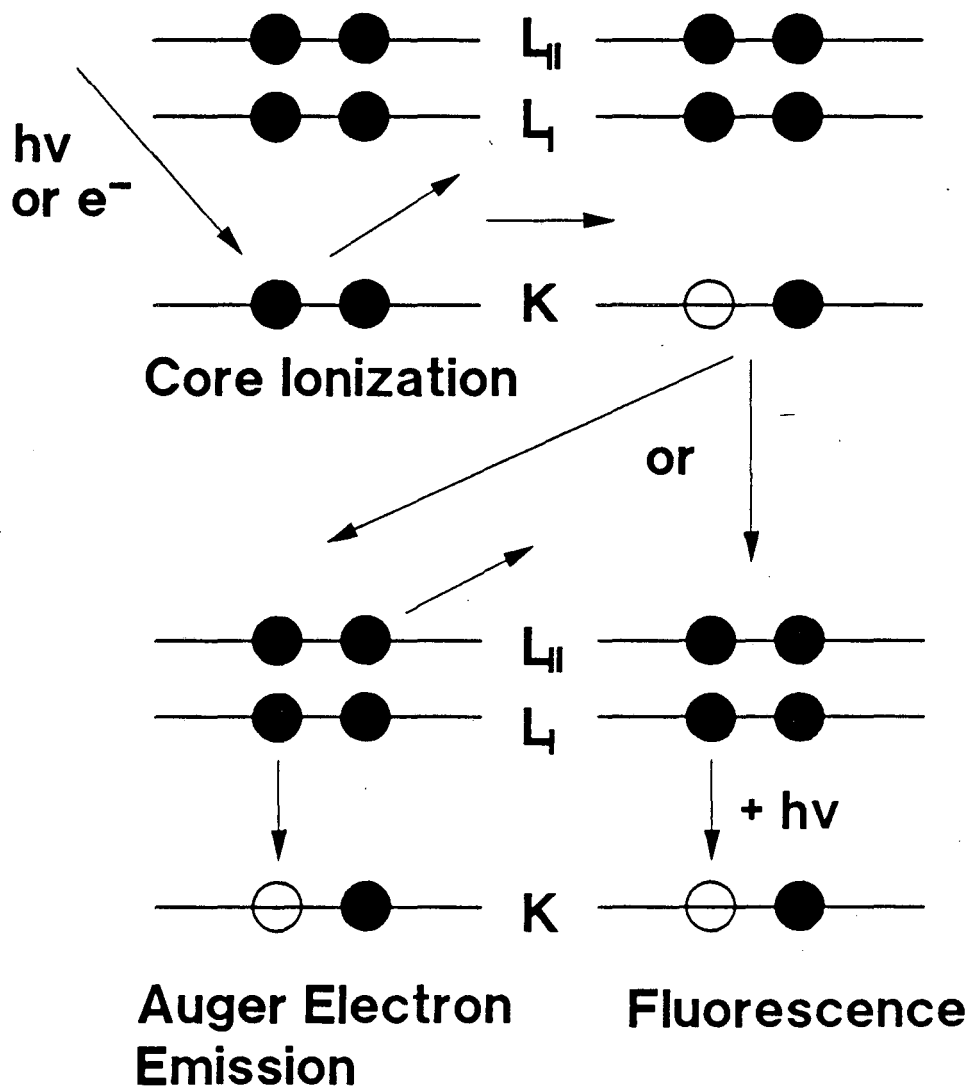


Figure 2.2. The Auger process. A core electron is removed (in this thesis by a 2 keV electron), creating a vacancy. This vacancy is filled with by a higher energy electron, which releases energy. This energy can be released by the emission of a photon or by the ejection of a valence electron.

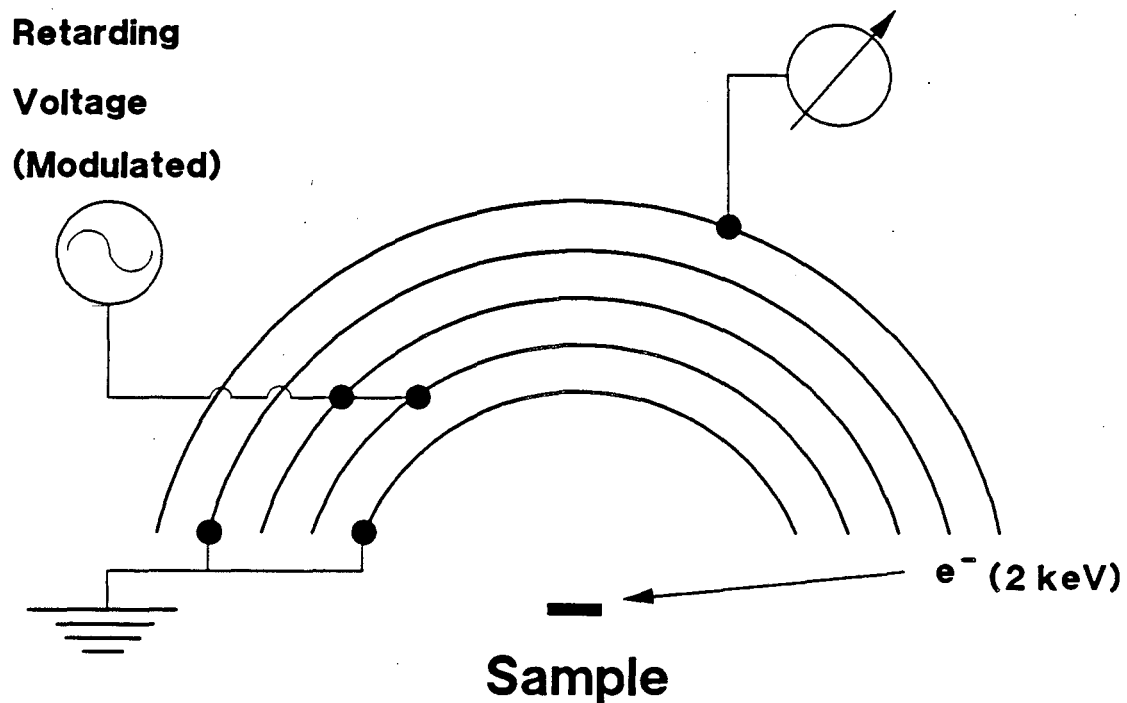


Figure 2.3. A schematic diagram of a retarding field electron energy analyzer (RFA). Auger electrons leaving the sample are retarded a potential applied to the second and third grids of the RFA, so that only electrons with energies greater than the retarding energy are detected. The retarding voltage has a sinusoidal signal superimposed on it to permit phase sensitive detection and differentiation of the signal.

Auger Electron Spectroscopy

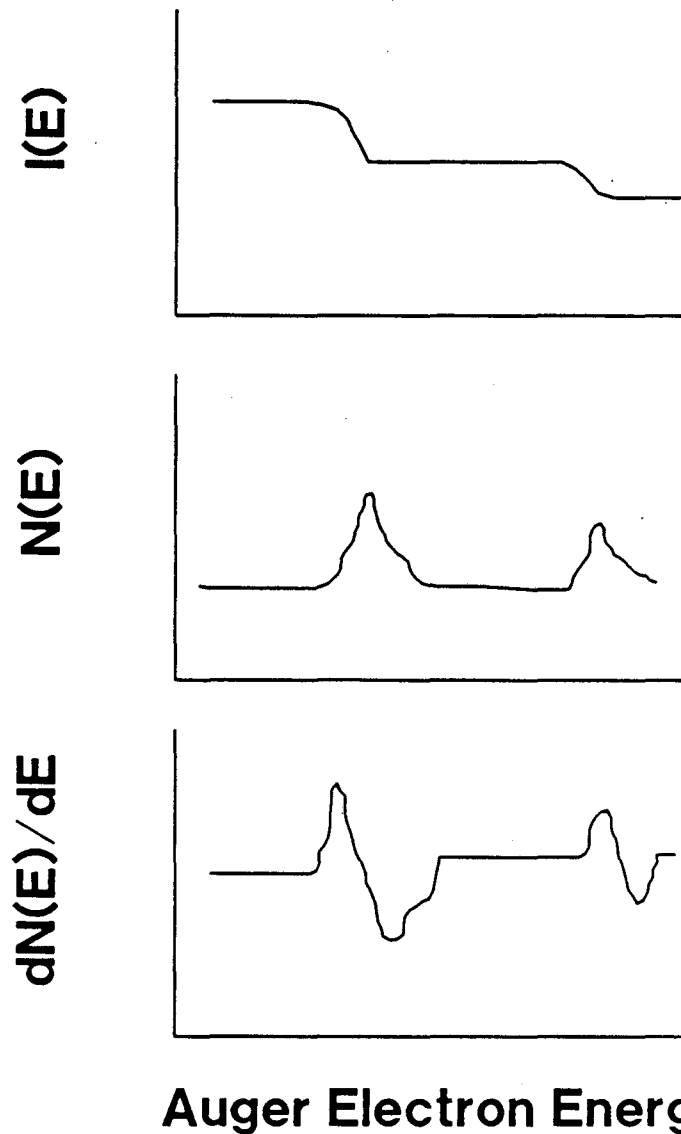


Figure 2.4. The differentiation of the Auger signal. Data from a RFA is obtained as an electron current which decreases with increasing retarding energy. The energy spectrum is differentiated twice, once to yield $N(E)$ vs. E , and again to produce the "first derivative" spectrum common in AES.

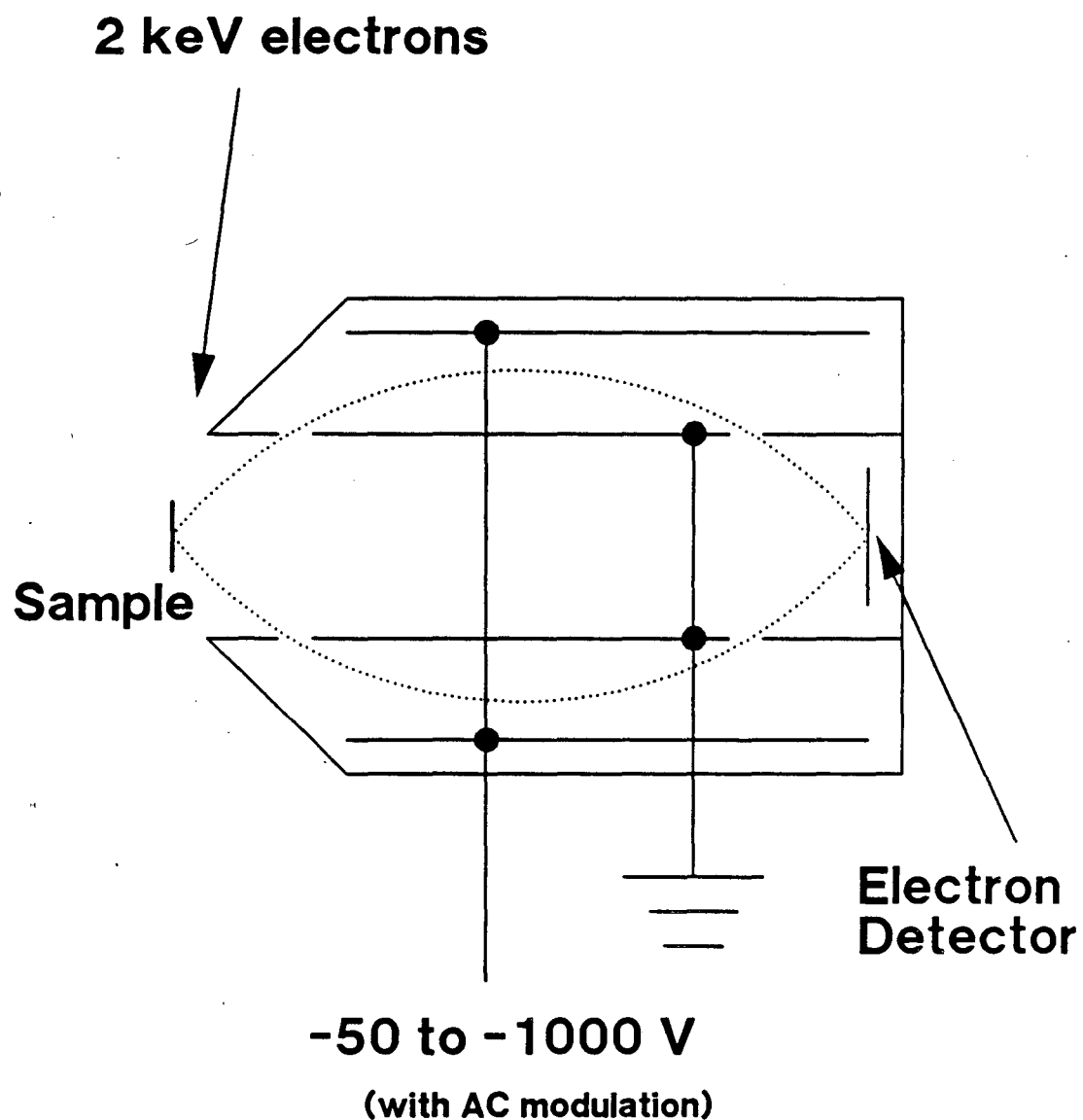


Figure 2.5. A diagram of a cylindrical mirror electron energy analyzer (CMA). Only electrons within a narrow energy range reach the detector. The potential of the outer cylinder contains an AC rider to permit differentiation of the $N(E)$ vs. E spectrum provided by the CMA.

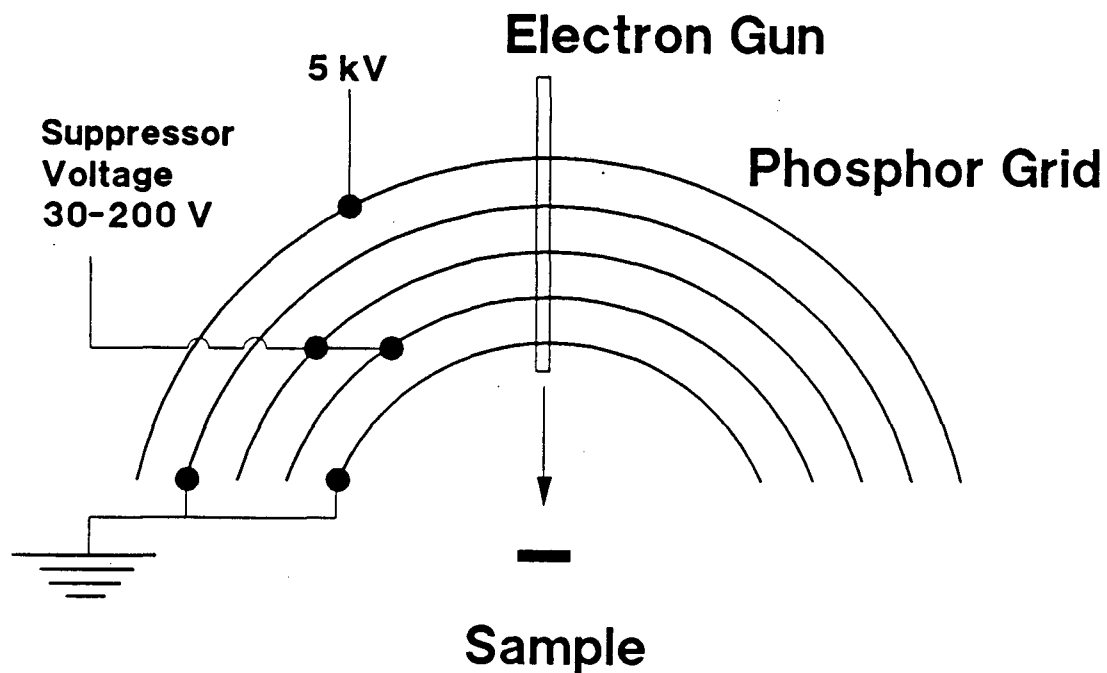


Figure 2.6. The RFA, configured to detect low energy electron diffraction patterns. The potential of the second and third grids retards any electrons not diffracted elastically from the surface. Elastically diffracted electrons are accelerated to a phosphor grid, where they can be observed and photographed.

3. THE FORMATION OF CoSi_2

3.1. INTRODUCTION

The reactions between metal thin films and silicon to form silicides is of practical importance because of the use of silicides as contacts in semiconductor devices. In the case of the late transition metals, the metal-rich silicide (M_2Si) forms first. After further reaction at higher temperatures, the thermodynamically most favorable (i.e. richest in Si) mono-or disilicide phase forms. Rules predicting the first silicide phase to form in these metal silicon reactions, while fairly successful, are empirical and there is a lack of a fundamental understanding of the processes involved.^{1,2} Increasing importance is being given to the role of surface free energy in understanding these phase changes.³ Studies of the reaction between Co and Si to form CoSi_2 are reported in this Chapter, including an investigation into the role of interfacial impurities between a Co film and a Si(111) substrate.

The effect of impurities between the metal film and the silicon substrate has received little attention. Interfacial impurities can act as diffusion barriers that slow the reaction of the metal and silicon, either changing the sequence of silicide formation or inhibiting the reaction completely. Impurities also alter the interfacial free energies of the metal-silicon system, which might change the order of silicide formation by changing the energy necessary for different silicide phases to nucleate. The effects of impurities on the Co-Si reaction

were studied in ultra-high vacuum (UHV, $<2 \times 10^{-10}$ Torr), an environment which permits the preparation of atomically clean interfaces as well as interfaces containing controlled amounts of impurities.

In the Co/Si system, most researchers report the sequence of silicide formation to be Co_2Si , CoSi , CoSi_2 ,^{4,5} with others claiming that the growth of Co_2Si and CoSi is simultaneous rather than sequential.^{6,7} As these experiments were carried out in only high vacuum (10^{-6} to 10^{-7} Torr), it is quite likely that impurities in the deposited films or at the interface have affected the order of silicide formation.

The final product of the reaction of a thin Co film on a Si substrate was CoSi_2 , a material that has been studied extensively because of its epitaxial growth on Si(111). CoSi_2 forms the highest quality epitaxial film of the known epitaxial silicides, as well as having the lowest resistivity.⁸ These properties not only make CoSi_2 a promising metallization material for smaller, faster semiconductor devices but also permit fabrication of vertically integrated devices such as the metal base transistor.^{9,10,11,12,13}

The effect of oxygen on the reaction between cobalt and silicon was studied by oxidizing the Si(111) substrate before Co deposition. The role of interfacial oxygen in this system is of practical importance because the surface of a clean, oxide-free Si wafer will be oxidized immediately to SiO_2 upon exposure to atmospheric oxygen. Any exposure of a silicon wafer to atmosphere before metal deposition will therefore result in an oxidized interface. This will be the case for processes that do not remove the SiO_2

layer in the same vacuum chamber used for metal evaporation. Any reaction between the metal film and the silicon substrate then depends on the ability of the metal to penetrate the surface oxide. The effect of interfacial nitrogen on the reaction between Co and Si(111) studied by exposing the Si surface to nitrogen before Co deposition. Nitrogen contamination is not a practical difficulty in silicon processing, since N_2 will not react with silicon surfaces below 1100°C . Instead, nitrogen was chosen as an interfacial dopant to serve as a comparison to oxygen.

These experiments were carried out in ultra-high vacuum to permit not only the precise compositional control of the Co-Si interface, but also the use of surface-sensitive electron spectroscopies to characterize the system. In addition, CoSi_2 films require an atomically clean Si(111) substrate for optimal epitaxial growth, a condition most easily satisfied in UHV. The thinness of the initial cobalt films ($<50 \text{ \AA}$) and the subsequent silicide films ruled out the use of bulk techniques such as Rutherford backscattering spectroscopy and X-ray diffraction for characterization. Auger electron spectroscopy (AES), used in these experiments, is only sensitive to the topmost atomic layers, and so is able to provide information about these thin films. The lineshapes and sizes (peak-to-peak heights) of the Auger peaks provide chemical and compositional information about the near surface region. However, the surface sensitivity of AES unfortunately limits the information to be gained in these thin film reactions because AES cannot probe the buried layers that lie further than about $20 \text{ \AA}$ from the surface. The epitaxial nature of CoSi_2

allowed the use of LEED to examine the surface crystallinity, providing information about the order of the surface and the presence of any surface reconstructions.

The initial interaction between Co and Si(111) was studied by slowly evaporating Co on a room temperature Si(111) substrate. The reaction between Co and Si at high temperatures was studied by depositing a thicker Co film on Si(111) and heating the system to at least 700°C. The role of interfacial impurities was investigated by evaporating Co on a surface modified with either oxygen or nitrogen and again heating to over 700°C. Auger electron spectroscopy was used to characterize both the initial interaction between the Co and Si, and the reaction between Co and Si at elevated temperatures, both for clean and modified Co-Si interfaces. The lineshape of the Si(LVV) AES peak gave important information about the chemical state of Si near the surface, which was affected by the reaction with Co and also by the presence of oxide and nitride. The effect of interfacial impurities on the epitaxy of the final CoSi_2 films was examined using low energy electron diffraction (LEED).

3.2. RESULTS

3.2.1. Clean Silicon

To probe the initial interaction of Co with the Si(111) substrate at room temperature, Auger spectra were recorded as a function of Co coverage. The initial Si surface displays the Si(111) 7×7 reconstruction in the LEED pattern prior to Co evaporation. Figure 3.1 shows the AES of this Si substrate. Co was deposited at a rate of ca. 1 Å/min, as measured by a quartz microbalance. Every 2 minutes the Si was rotated away from the evaporator to record an Auger spectrum until 16 Å of Co had been deposited. The heat produced by the evaporator caused the Si temperature to increase from room temperature to 70°C over the course of the experiment. The shape of the Si (92 eV) AES peak does not change appreciably during the initial stages of Co uptake (Figure 3.2). The dip in the AES at 72 eV and the inflection at 90 eV gradually disappear with the deposition of Co. This evolution of the lineshape of Si (92 eV) clearly indicates that the deposition of thin films of cobalt changes the chemical state of silicon.

Figure 3.3 shows the change in Co and Si Auger peak-to-peak heights with the deposition of Co. The initial deposition of Co results in little change in the Co peak height. After the deposition of 20 Å of Co, however, the Si Auger peak height has decreased in size to one third its original height and is smaller than the Co peak. It was questionable at best whether any breaks were seen in the slopes of the Co and Si Auger peak-to-peak heights as a function of Co coverage; apparent breaks in the Co peak heights were not matched by corresponding breaks for Si. The lack of regions of constant slope in the peak-to-peak heights of the Co or Si Auger peaks as a function

of Co film thickness shows that cobalt film growth does not occur layer-by-layer on Si(111), a result consistent with the chemical interaction between Co and Si observed in the Auger lineshape of Si.

The reaction between Co and Si at elevated temperatures was studied by evaporating a Co thin film onto a Si(111) substrate and heating the sample at 12°C/s to at least 600°C. The AES of a 35 Å Co film is given in Figure 3.4, displaying the Co AES transitions at 53, 656, 716, and 775 eV. The small 92 eV peak is due to Si and originates from Si dissolved in the overlying Co film. This peak presumably hides the less intense 95 eV Co peak, which is not observed.

Figure 3.5 displays the changes in Auger lineshapes and peak-to-peak heights for both Co (53 eV) and Si (92 eV) as the system is heated. The small, sharp spikes that appear at varying energies are experimental artifacts caused by the temperature controller. The most obvious feature of these spectra is the decrease in the Auger peak-to-peak heights for Co and the corresponding increase for Si. Less obvious is the change in the shape of the Si peak. Little change is seen until 200°C, when the peak height starts to increase. As heating continues, the inflection at 72 eV becomes more pronounced and between 400 and 500°C a peak grows in at this energy. The shape of the top of the Si peak also changes with heating, becoming thinner at higher temperatures and forming a barely detectable inflection point at ca. 90 eV.

The final AES (Figure 3.6), taken after heating to 692°C, contains both the dip at 72 eV and a weak inflection at ca. 90 eV. The low energy Co AES peak is still visible at 53 eV, but the higher energy Co peaks have almost disappeared in the background noise. Not shown is the LEED pattern of this surface, which shows a 7 x 7 reconstruction of the bulk unit cell.

The evolution in Auger peak-to-peak heights as a function of temperature is shown in Figure 3.7 for Co (53 eV) and Si (92 eV). Just as with the Si lineshape, little change is observed in the Co and Si peak heights below 200°C. Near 200°C the Si peak height grows, accompanied by a decrease in the height of the Co peak. The Co peak height shows a plateau between 300 and 400°C and another above 450°C. No plateaus at temperatures above 200°C are seen in the Si peak heights, although the slope of the curve decreases with temperature. The changing shape of the Si (92 eV) peak again indicates the changing chemical state of silicon as a function of temperature. The enrichment of the near surface region in silicon and the presence of plateaus in the cobalt peak height suggest the formation of cobalt silicides in the near-surface region, a conclusion supported by the observed change in the chemical state of silicon.

This experiment was repeated using a thinner Co film on Si. The evolution of the peak-to-peak heights for a 15 Å Co film on Si(111) is shown in Figure 3.8. The same behavior is observed as for the thicker film, though the reaction seems to start at lower temperatures. The same plateaus are seen for Co (53 eV), and again none are present for Si (92 eV).

3.2.2. Oxygen

To study the effect of interfacial dopants on the formation of silicide phases, the Si(111) surface was oxidized before Co deposition. The oxidation was done by exposing the Si to 1 atm. of O₂ for 3 minutes. The Auger spectrum of this oxidized Si is given in Figure 3.9, showing dips in the Si peak shape at 65, 77, and 92 eV. The Auger peak of clean silicon occurs at 92 eV; the dips at 65 and 77 eV are due to oxidized silicon. A large oxygen signal is seen in the Auger spectrum, along with a significant amount of carbon.

After 27 Å of Co were deposited on this oxide surface, the Auger spectrum which appears in Figure 3.10 was obtained. The C and O present in this spectrum are most likely contaminants of the deposited Co film rather than dissolved silicon oxide, since only a tiny Si AES signal is seen.

The sample was then heated (12°C/s) and the Auger spectra of the Co and Si peaks recorded continuously (Figure 3.11). Very little change in the Co and Si peak-to-peak heights or lineshapes is observed until about 200°C, the same behavior seen in the unmodified Co/Si(111) system. The Si peak increases in size but does not lose its oxide character until 650°C, judging by the presence of the 65 eV feature of the Si peak. At this point the temperature was increased manually so that the heating rate was no longer linear with time.

The change in the surface composition of this system with heating is shown in Figure 3.12. No plateaus are seen for Co. The Si peak height passes through a local maximum around 450°C, after which it decreases slowly until 650°C. Heating above 650°C caused the peak heights of both the Co and Si to increase, with the larger increase for Si. These peak height increases occur at the same temperatures as the disappearance of the surface oxide.

The final Auger spectrum of this system taken after heating past 700°C, is displayed in Figure 3.13. No oxygen is present, and the shape of the Si peak does not suggest any oxide character. The Si lineshape has a dip at 72 eV. The LEED pattern obtained from this surface (not shown) indicates a 7×7 reconstruction.

3.2.3. Nitrogen

Exposure of Si(111) to NO, NH₃, or N₂ at elevated temperatures results in nitridation of the surface.^{14,15,16} It must be noted that N₂ does not react with Si below ca. 1100°C: either predissociation using a hot filament or sputtering (ionizing and accelerating N₂ at the Si) is required. The sputtering route was chosen for experimental ease. The N₂ was accelerated to an energy of 800 eV, with the resulting 4.7 μ A beam striking the Si at an angle of 11.5°. The N₂ pressure during sputtering was 6×10^{-5} Torr.

The AES taken after nitridation is shown in Figure 3.14; as is evident, the surface of the Si wafer contains C and O as well as N. Annealing at 750°C and ultimately at 900°C resulted in a change in the low energy Si AES (LVV) lineshape and a relative increase in the amount of O present to the point where the O peak was larger than the N, disregarding relative AES sensitivities (Figure 3.15). The LEED pattern obtained after heating to 900°C closely resembles the " 8×8 " structure reported for Si(111) surface nitrides (≤ 1 ML) by two research groups,^{14,15} though one group (Schrott et. al.) report the 8×8 structure only when the C impurity level is below 0.02 ML.

This nitridation was followed by the deposition of 34 Å of Co and subsequent annealing at 12°C/min. while again monitoring the AES from 30-100 eV. Figure 3.16 shows the effect of annealing temperature on the Si and Co peak-to-peak heights, each of which passes through three plateaus. These regions resemble the three plateaus of the clean, undoped Co/Si system, and are due most likely to Co_2Si , CoSi , and CoSi_2 . The LEED pattern obtained after annealing at 730°C was 1×1 (i.e. unreconstructed) with broad, fuzzy spots, indicating a decrease in the order of the surface.

Next, the nitridation was repeated with the goal of increasing the amount of surface nitride and decreasing the C and O impurity levels. Flushing the chamber with ca. 10^{-4} Torr N_2 and evacuating to 3×10^{-7} Torr with the turbo pump before refilling and sputtering with N_2 was effective in reducing the amount of impurities. Better aim of the sputter beam increased the surface nitrogen content, as seen in Figure 3.17. Annealing the sputtered

surface to 750°C increased the N/Si AES ratio and the "nitrided character" of the Si, judging by the 83 eV dip in the Si AES^{15,16} (Figures 3.18 and 3.19). No LEED pattern was seen, consistent with a thick, disordered nitride layer.

Figure 3.20 shows the Auger spectrum of 30 Å of Co that was deposited on this nitride. Next, the AES annealing experiment was repeated; following the AES lineshape evolution in the range of 30-100 eV results in the spectra shown in Figure 3.21. No plateaus were observed in the plot of Co and Si Auger peak-to-peak heights as a function of temperature, except perhaps for the formation of CoSi_2 above 500°C (Figure 3.22). The final AES (Figure 3.23) shows large C and O impurities of the same magnitude as the N.

Further annealing of the nitrided silicide/Si system at temperatures less than 750°C has little effect except for a slight increase in the amount of N compared to O and C. After 800°C this effect becomes more pronounced, and 900°C is sufficient to remove all O. The C is unchanged and the N surface concentration is much higher, though the 83 eV nitride feature of the Si AES is less pronounced than before (Figure 3.24). LEED shows a 3-fold arrangement of broad, oblong spots against a high background, and vaguely resembles the "quadruplet" structure reported for Si-N.^{14,15}

3.3. DISCUSSION

3.3.1. Clean silicon

The early stages of Co deposition on a Si(111) substrate involve chemical changes, as demonstrated by the change in the Si (92 eV) lineshape. Neither regions of constant slope nor sharp breaks occur in the peak-to-peak heights of the Co or Si Auger peaks as a function of Co thickness during Co uptake, indicating that film growth is more complex than simple deposition of successive Co layers.¹⁷ These results suggest that Co deposition results in intermixing and possibly phase formation between the Co and Si during the arrival of the first Co layers.

Room temperature reaction between small amounts of Co and Si(111) has been reported by many researchers, most of whom describe the formation of a CoSi_2 -like phase after the deposition of 4 Å or less of Co. This phase has been characterized by high resolution core-level photoemission spectroscopy,¹⁸ LEED, angle-resolved ultraviolet photoelectron spectroscopy, and X-ray photoelectron spectroscopy,¹⁹ surface electron energy loss fine structure,²⁰ and resistivity and Hall effect measurements.²¹ Gibson et. al. claim, however, that the initial deposition of Co forms a hexagonally distorted form of Co_2Si , based on transmission electron microscopy and diffraction experiments.²²

As more Co is deposited, the formation of the CoSi_2 -like phase becomes limited by diffusion at room temperature, and the phase is covered by a Co film. Considerable intermixing still occurs, however, as demonstrated by the existence of the Si (92 eV) AES peak after Co deposition. This peak

is still found after the deposition of 35 Å of Co, a thickness sufficient to block essentially all of the Si (92 eV) Auger electrons that originate from the substrate. The solubility of Si in Co (13 atomic % at 700°C²³) suggests that most of this Si has segregated to the sample surface, instead of being dissolved in the Co film.^{20,21}

The formation of silicides as a function of temperature was studied by heating the Co/Si sample and monitoring the Co (53 eV) and Si (92 eV) Auger peaks. The surface sensitivity that makes AES such a useful tool for surface science limits the information to be gained here, since AES cannot probe buried phases. The changes in the peak shapes of Si as a function of temperature reflect the changing chemical state of Si as Co and Si react to form silicides. No plateaus are observed in the evolution of the Si peak-to-peak heights as a function of temperature, except perhaps for an initial peak that disappears above 200°C. The Co peak-to-peak height passes through three plateaus: from 300-400°C, above 450°C, and the same initial plateau under 200°C observed for Si.

The change in Si lineshapes, together with the plateaus in the Co peak heights, suggests the formation of various silicide phases. The enrichment of the system in Si is consistent with the sequential formation of Co₂Si, CoSi, and CoSi₂, which are the only Co silicide phases known. This conclusion was also reached by D'Avitaya et. al., who observed three plateaus for both Co and Si and attributed them to Co₂Si (350-400°C), CoSi (450-550°C), and CoSi₂ (600°C).⁵ The formation of these silicides at similar temperatures has

also been reported for thicker films by researchers using bulk characterization techniques (Rutherford backscattering spectroscopy and X-ray diffraction).

If the plateaus seen for the Co Auger peak height during annealing are real, then perhaps the absence of plateaus for Si can be explained by the larger width of the Si Auger peak versus the Co peak: voltage spikes and magnetic fields due to the temperature controller become more likely for peaks taking longer to scan. The shape of the Si (92 eV) peak is also dependent on the chemical state of the Si, and a change in peak shape would be expected to affect the peak height.

The final LEED pattern for a CoSi_2 film is unreconstructed (1×1). In the annealing experiments described in this chapter, heating was never stopped so that a CoSi_2 film with a 1×1 LEED pattern could be produced. Annealing past the formation temperature of an unreconstructed CoSi_2 surface (ca. 550°C) led to an enrichment of the surface region in Si and a 7×7 LEED pattern. This LEED pattern has been attributed both to a post-silicide phase²⁴ and to regions of bare silicon between CoSi_2 (1×1) islands that contribute a Si(111) 7×7 pattern.⁵ The surfaces of CoSi_2 films, both reconstructed and unreconstructed, will be discussed in the next chapter.

3.3.2. Oxygen

To observe the effect of impurities, the Si(111) substrate was oxidized before deposition of the Co layer. The resulting Auger spectrum shows that

both unoxidized Si and SiO₂ are present on the surface after the oxidation. Evidence for the existence of SiO₂ comes from the dips in the AES at 65 and 77 eV which have been reported for SiO₂,¹⁶ with the strong 92 eV Si peak indicating unoxidized Si. The coexistence of both Si and SiO₂ in the Auger spectrum suggests that this oxide layer is either not continuous across the silicon surface, or that it is sufficiently thin to permit the transmission of Auger electrons from the substrate. Surface carbon is also present on the oxidized Si surface. Joyce and Neave also found carbon deposition to accompany the oxidation of Si(111).²⁵ They attributed it to the production of CO during oxidation, which then adsorbed and decomposed on the Si surface, though others report that CO does not adsorb on Si at low temperatures.²⁶

The Auger spectrum after the deposition of Co on an oxidized Si(111) surface showed that Si did not segregate to the surface of the Co film at room temperature, as was seen after the deposition of Co on clean Si(111). The diffusion of Co into the Si was also slower than in the unoxidized Co/Si system, as shown by the higher temperatures required for Co diffusion into the bulk. This slower diffusion is consistent with the much larger heat of oxidation of Si compared to Co. Co is unable to compete with Si for oxygen and must diffuse into the Si substrate through gaps in the surface oxide. No plateaus were seen for either Co or Si AES peak-to-peak heights as a function of temperature. The lack of plateaus reflects an absence of complete silicide phase formation at the surface of the sample. If silicide phases formed, then this occurred too far from the sample surface to be

detected by AES.

The order of formation of the various silicide phases cannot be elucidated from this experiment, yet the decrease in rate of Co diffusion into the Si bulk is consistent with observations of simultaneous $\text{Co}_2\text{Si}/\text{CoSi}$ growth; as the Co flux to the active Co_2Si -forming interface is restricted by the oxide, the temperature rises sufficiently to permit formation of CoSi between Co_2Si and Si. The presence of an interfacial oxide may be the explanation for the simultaneous formation of Co_2Si and CoSi reported by researchers using non-UHV conditions.^{6,7}

From the AES it was seen that the surface Si remained oxidized until ca. 650-700°C, when the oxide presumably sublimed as SiO, leaving CoSi_2 . The mechanism of oxide removal is inferred by analogy to SiO sublimation from Si, though there it occurs at 850-900°C. The final surface displayed the 7×7 surface reconstruction and enrichment in Si found in the overannealed silicide that resulted from the reaction between Co and a clean Si substrate. Auger spectra taken immediately after the removal of the surface oxide do not exhibit excess Si and suggest the 1×1 CoSi_2 phase. The following chapter explores possible routes to the 1×1 CoSi_2 surface by oxidizing a 7×7 CoSi_2 surface and subliming the oxide.

3.3.3. Nitrogen

The first attempt at nitriding the Si(111) surface resulted in a surface containing N, but also contaminated with C and O (Figures 14 and 15). This oxygen, and a comparison to the Si AES of Si_3N_4 , SiO_2 , and various Si oxynitrides of Hezel and Lieske¹⁶ suggest strongly that this nitrided surface is in fact an oxynitride. It appears likely that the N coverage is less than 1 ML, which is supported by the LEED data of Schrott and Wang.^{14,15} The LEED pattern obtained after annealing to 1250°C is a faint "8 × 8" whose fainter, higher order spots have been obscured by impurities. This is also consistent with a low N coverage, probably resulting from missing the Si with the sputter beam: the sputter gun merely served to dissociate the N_2 , and so the crystal was exposed to 0.05 L of N atoms.

No Si segregation to the top of the Co film was observed at room temperature in this nitrided system, the same result found for Co deposition on an oxidized Si surface. However, reaction of Co with this substrate resulted in the same sequential formation of cobalt silicide phases that occur on unmodified Si(111), indicating that diffusion in the reacting system was not drastically impeded. In addition, this submonolayer N coverage did not change the silicide order of formation by altering the interfacial free energies.

The second nitridation resulted in a much thicker, cleaner nitride layer. The improved aim of the sputter beam increased the amount of N_2 impinging onto the Si. Flushing the chamber with N_2 before sputtering displaced contaminants (H_2O , CO, CO_2) from the chamber walls and provided a purer N_2 environment for sputtering. The impurities (especially O) found in the

annealed Co/Si-N/Si sample must have come from the bulk of the deposited Co film, as they were not observed in the surface of the Si film nor on the initial Si - N surface. The Auger spectrum of the final surface bears a strong resemblance to the initial, nitrided (O-free) Si surface (Figure 3.17).

The evolution of the Co and Si peak heights for the sample with this thicker interfacial nitride closely resembled that for the Co/Si-O/Si system. Si_3N_4 , like SiO_2 , is thermodynamically very stable and serves as a diffusion barrier. Co, which is the primary diffusing species in the formation of Co_2Si in the unmodified system,²⁷ is unable to compete with Si for the interfacial N (or O) and is thus impeded in its diffusion into Si. This would explain the higher temperatures necessary for reaction and the absence of plateaus for the intermediate silicide phases, since unreacted surface Co might coexist with buried layers of CoSi or CoSi_2 .

3.4. CONCLUSIONS

The initial deposition of cobalt atoms on Si(111) resulted in a chemical change of the surface Si atoms, which was shown by the lineshape change of the Si(LVV) Auger peak. The presence of oxygen and nitrogen on the Si(111) surface also changes the shape of the Si peak. The characteristic changes produced by oxygen and nitrogen were useful in observing the high temperature reaction between Co and Si at an oxidized or nitrided interface.

The evolution of the Co and Si peak-to-peak heights for the initial deposition of Co on Si(111) indicates that the growth mechanism of Co is more complex than the formation of successive Co layers on a Si substrate. The Auger peak-to-peak heights of Co during the annealing of the Co-Si system also permitted the observation of plateaus, which were attributed to the formation of Co_2Si , CoSi , and CoSi_2 . An enrichment of the amount of surface Si of the final surface after heating to 700°C was seen in the AES. This Si-rich surface was shown by LEED to have a 7×7 reconstruction.

The presence of a surface oxide slowed the reaction between Co and Si to the point where no plateaus corresponding to silicide formation were observed. The thin oxide layer was sufficient to act as a diffusion barrier to slow the diffusion of Co. The formation of silicides then occurred under this oxide layer, where it could not be detected by AES. At high temperatures the oxide layer desorbed, leaving a CoSi_2 surface with excess Si, and a 7×7 LEED pattern. A thin nitride layer on the Si substrate also slowed the reaction between Co and Si, but AES still contained plateaus showing successive silicide formation. No plateaus were observed for the reaction between Co and a Si substrate containing a thicker surface nitride layer. The increased thickness of this nitride layer was sufficient to retard the diffusion of Co to the point that silicide formation occurred under the surface nitride. The effect of oxidized and nitrated interfaces to slow Co diffusion and prevent the formation of silicides at the surface may explain the reports of simultaneous Co_2Si and CoSi observed by RBS.^{6,7}

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AES of Si(111)

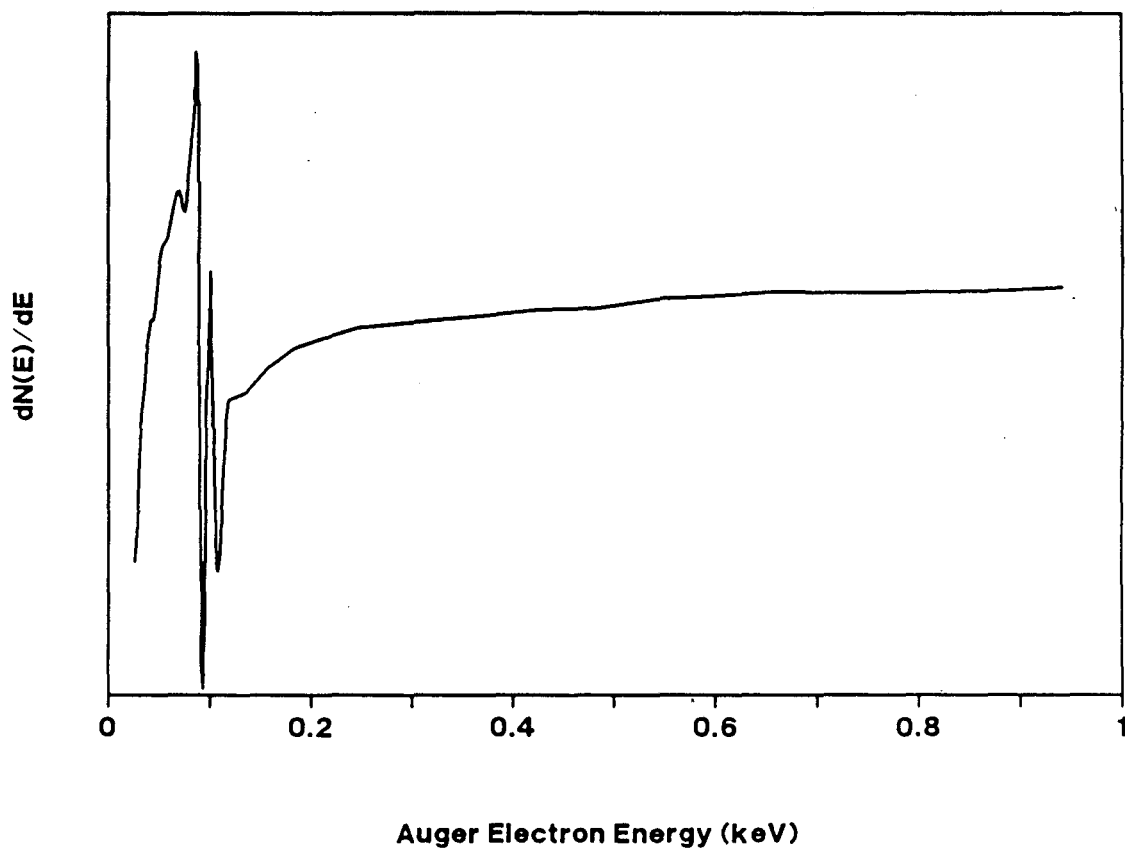


Figure 3.1. The Auger spectrum of a clean Si(111) substrate. The shape of the Si (LVV) peak is dependent on the chemical state of the near-surface silicon. The energy of this peak (92 eV for clean Si) also depends on the chemical state of the Si but is not affected as dramatically as the peak shape.

Co Uptake on Si(111)

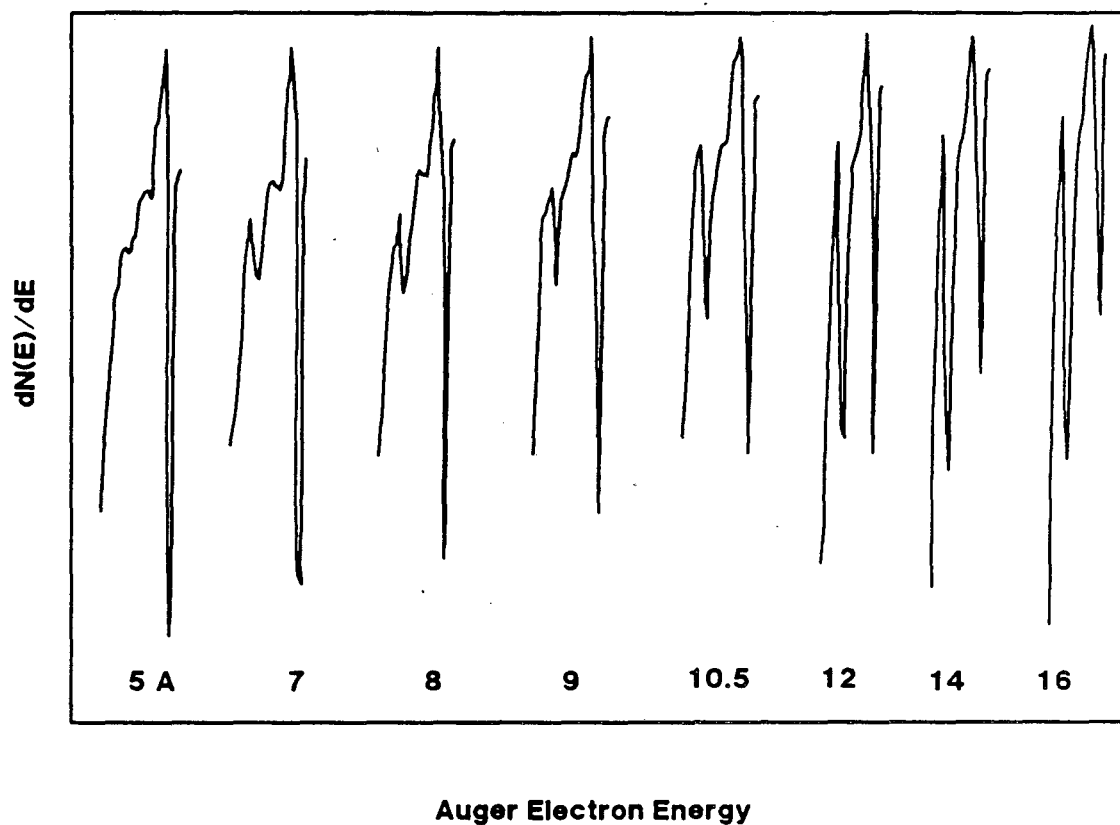


Figure 3.2. The evolution of the Co (53 eV) and Si (92 eV) Auger peaks during Co deposition on Si(111). The change in the Si lineshape reflects the changing chemical state of Si as Co is deposited.

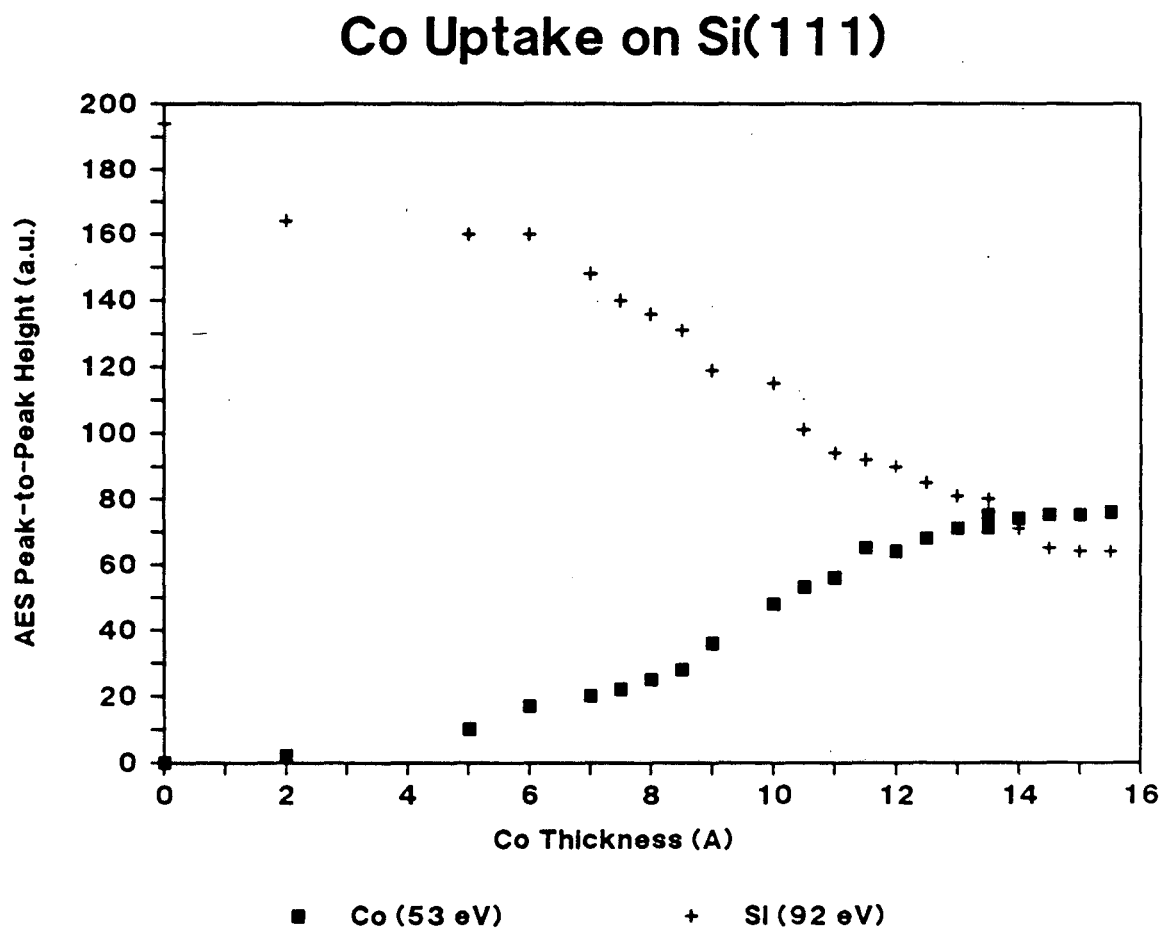


Figure 3.3. The uptake of Co on Si(111), showing the peak-to-peak heights of the Co (53 eV) and Si (92 eV) Auger peaks as a function of Co thickness.

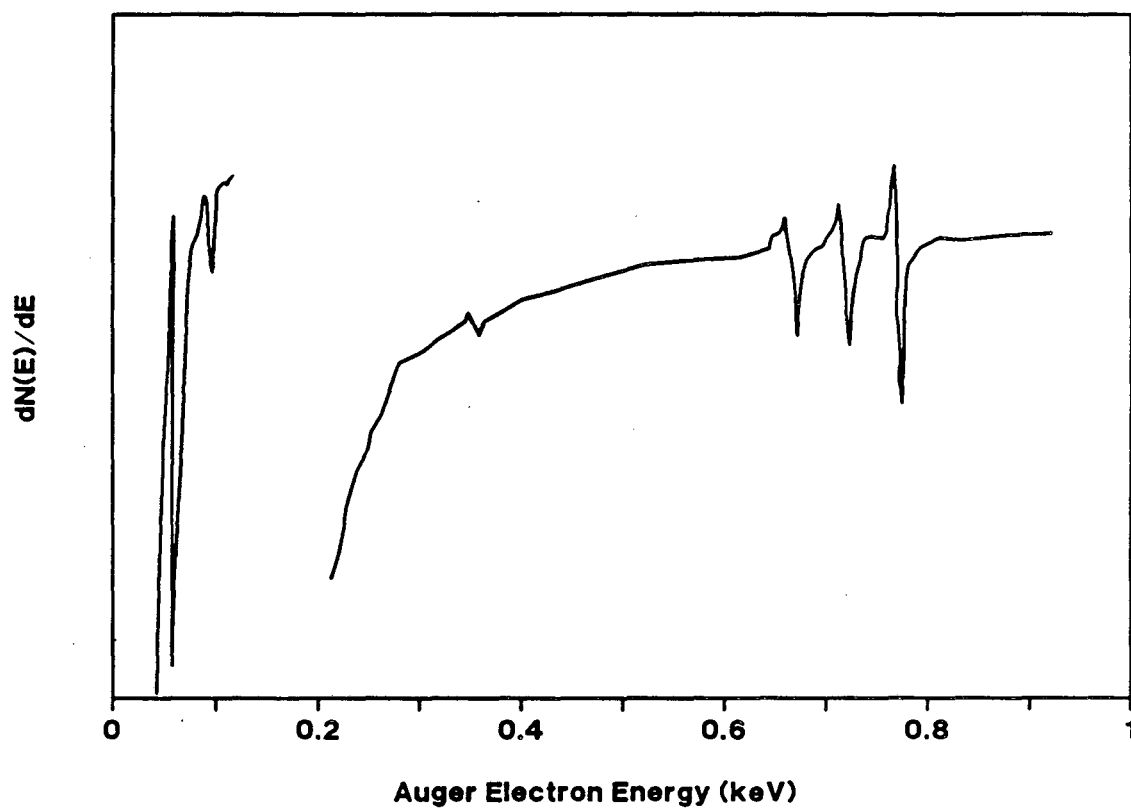
35 Å Co/Si(111)

Figure 3.4. The Auger spectrum of 35 Å of Co deposited on Si(111) before heating the sample. Note the presence of Si, indicating that Si exists near the surface even after the deposition of Co.

Evolution of Co/Si(111), Part 1

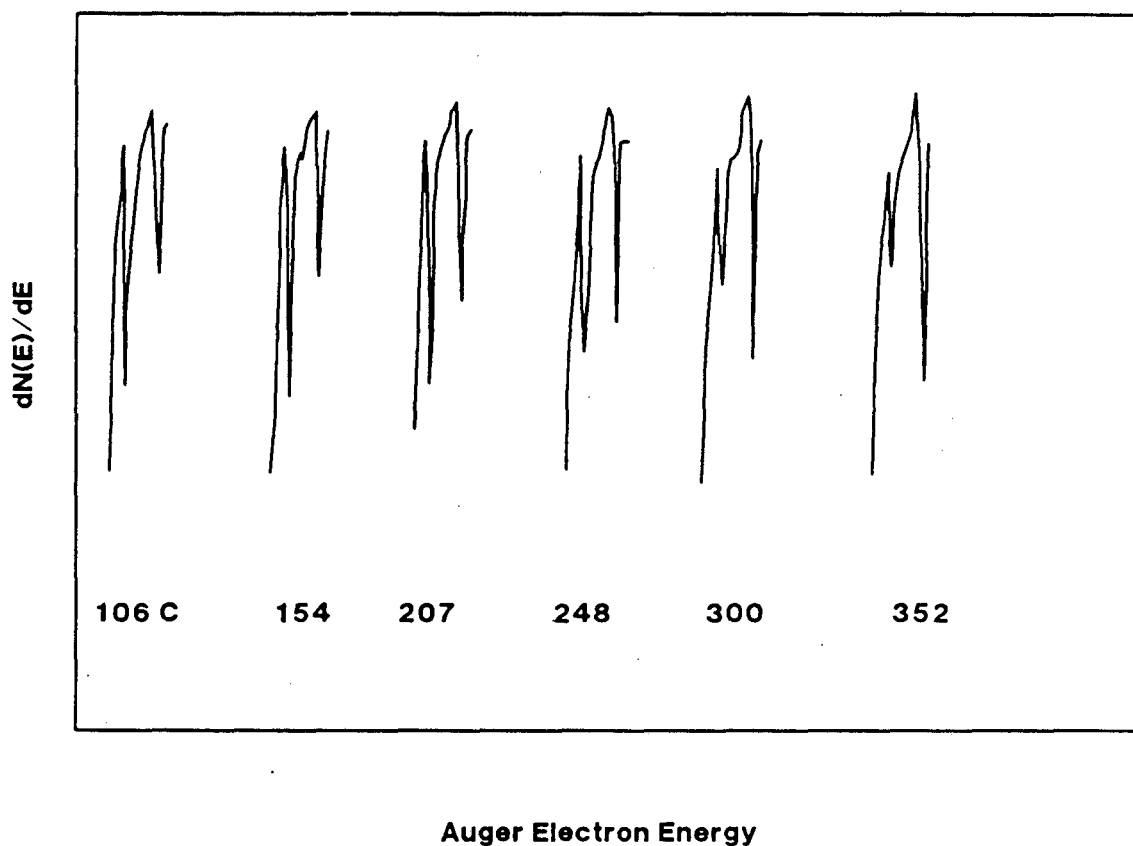


Figure 3.5.A. The change in Co and Si lineshapes as 35 Å of Co reacts with the Si substrate (Part 1). Temperatures (°C) at which spectra were taken are indicated under spectra.

Evolution of Co/Si(111), Part 2

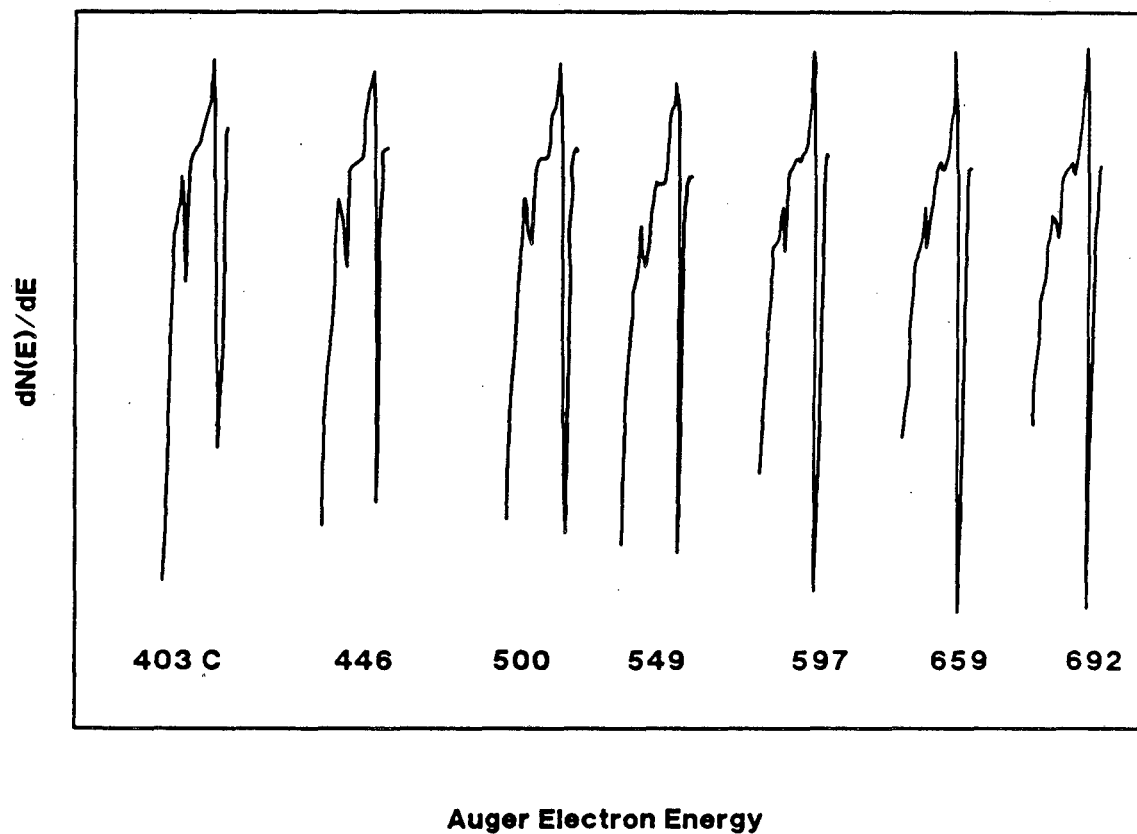


Figure 3.5.B. The change in Co and Si lineshapes as 35 Å of Co reacts with the Si substrate (Part 2). Temperatures are again indicated under spectra.

CoSi₂(111) Surface (7 X 7)

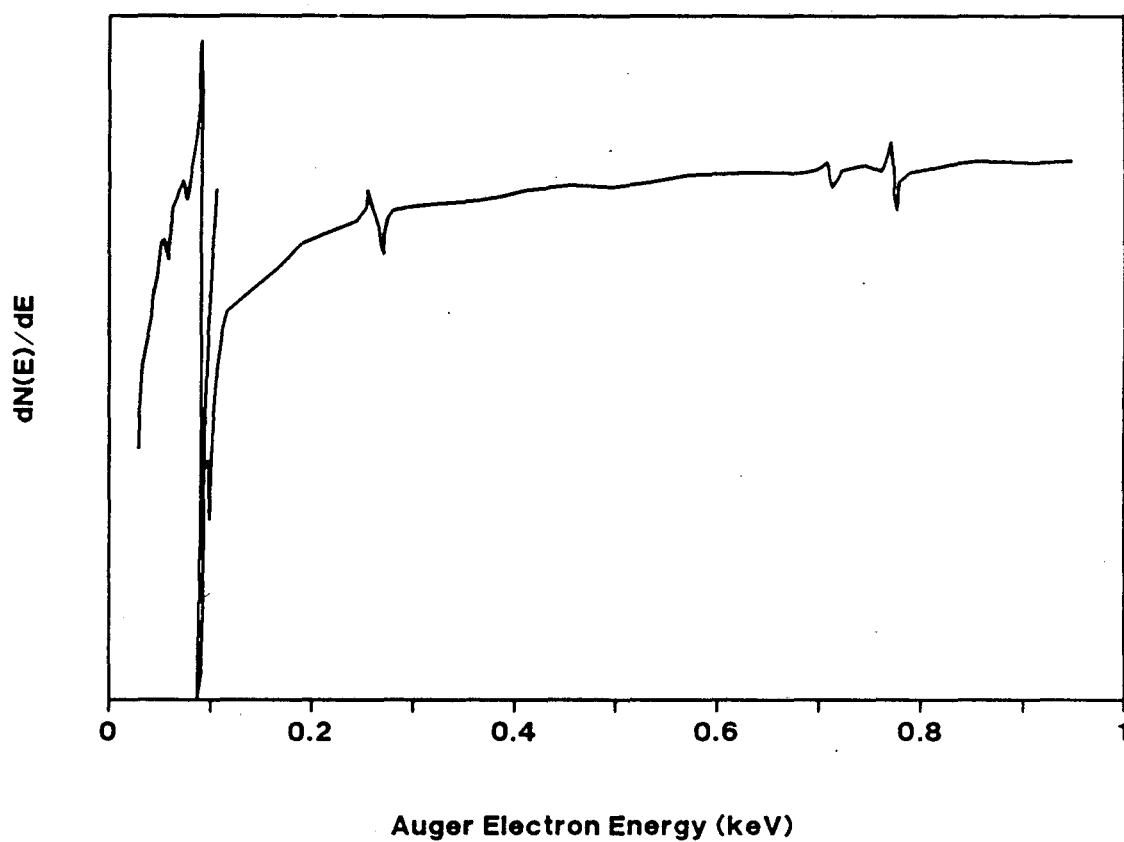


Figure 3.6. The final Auger spectrum after heating to 675°C. This surface displays a 7×7 LEED pattern.

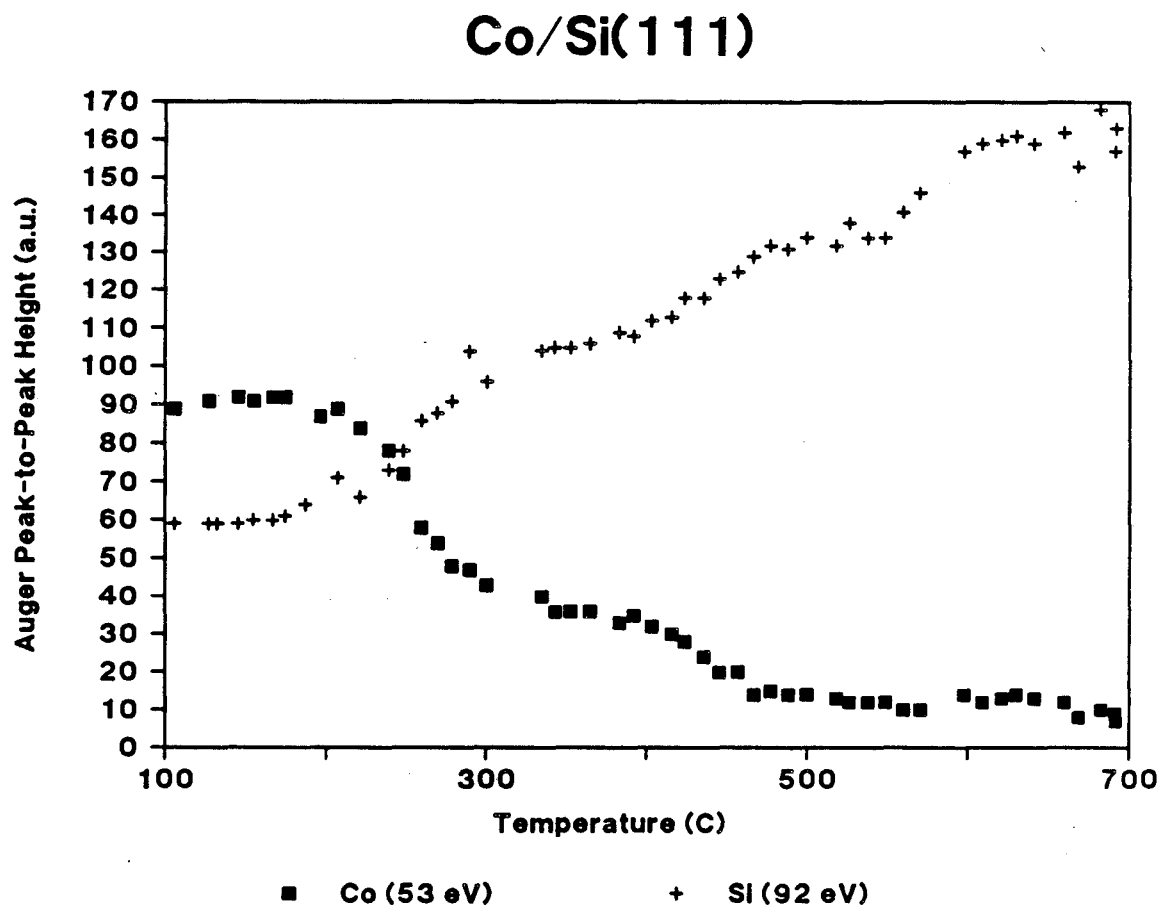


Figure 3.7. The change in composition of the near-surface region as a function of temperature, obtained by measuring the Co and Si Auger peak-to-peak heights.

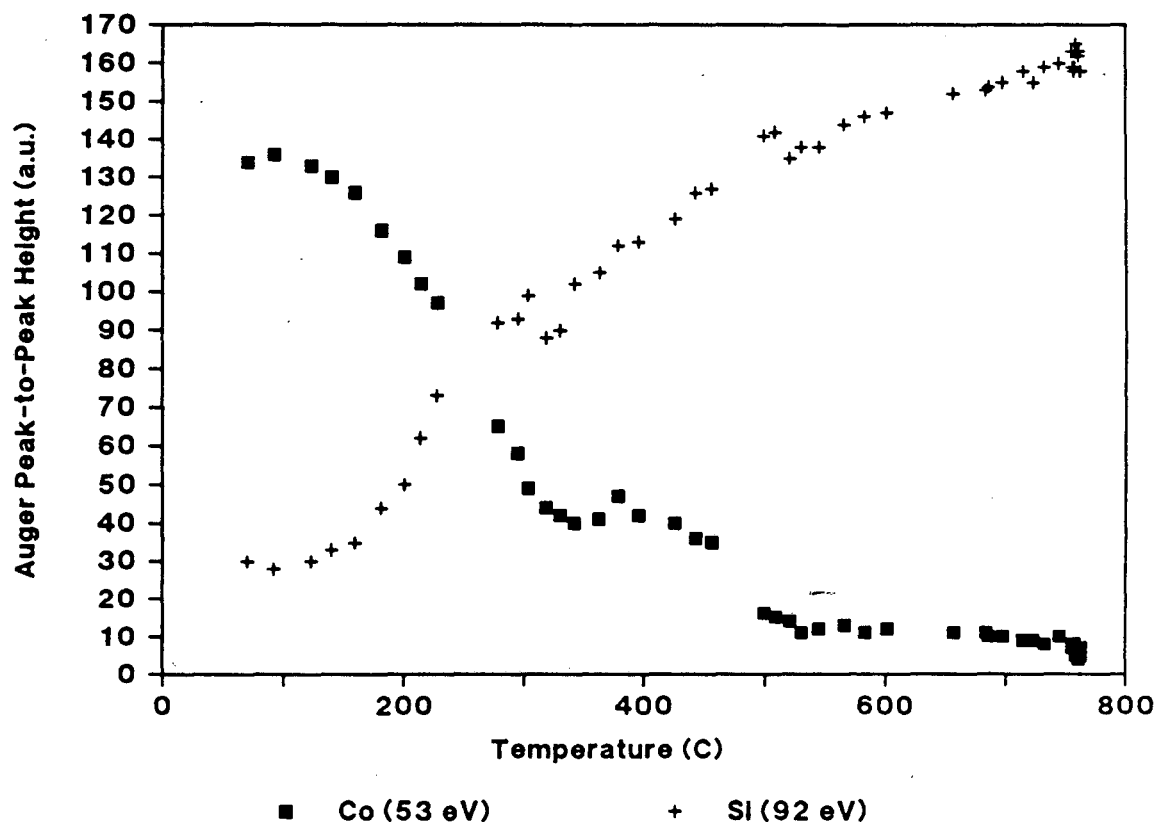
Co/Si(111)

Figure 3.8. The evolution of the surface composition as a function of temperature for a thinner (15 Å) Co film on Si(111).

Oxidized Si(111)

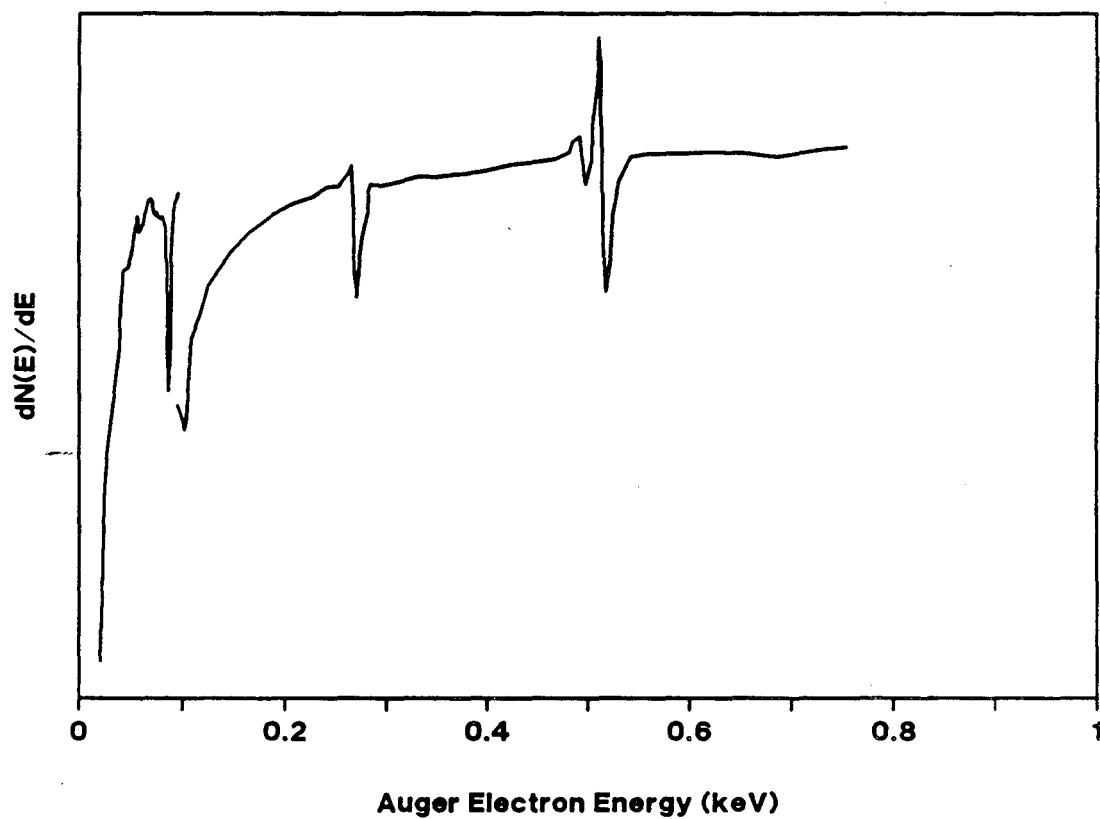


Figure 3.9. The Auger spectrum of an oxidized Si(111) surface, whose lineshape displays features of both oxidized and clean Si.

Co on Oxidized Si(1 1 1)

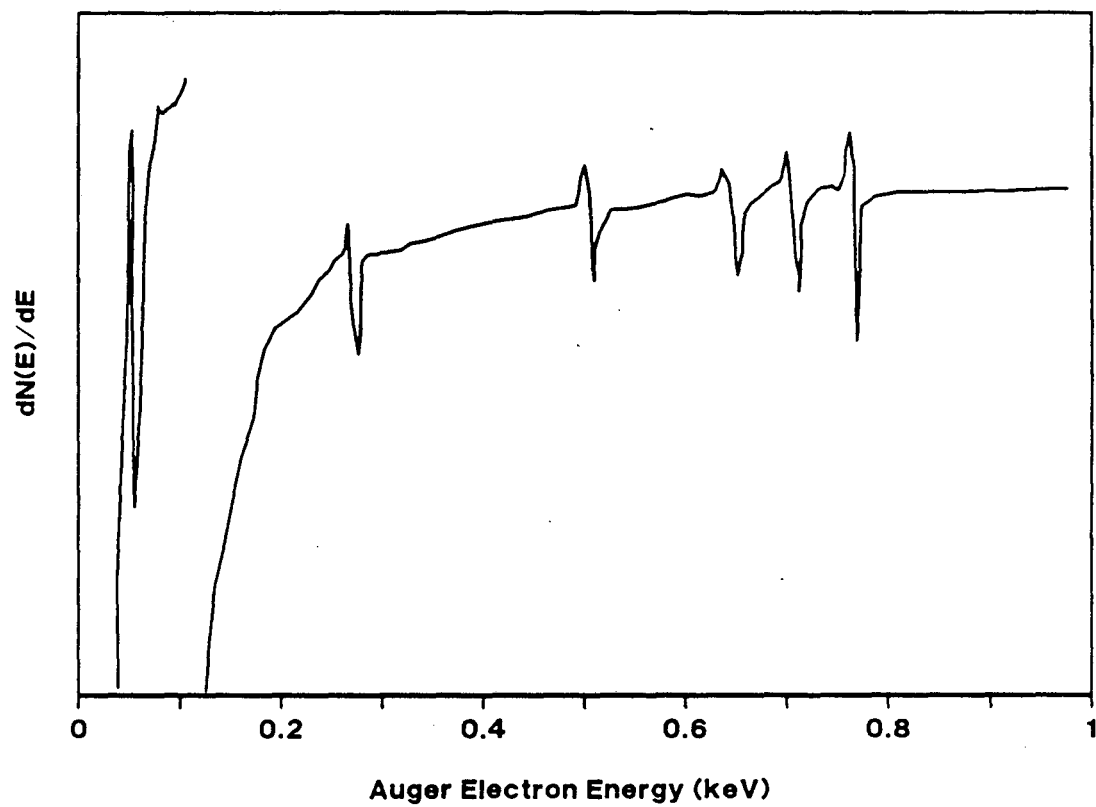


Figure 3.10. The Auger spectrum of 27 Å Co deposited on an oxidized Si surface (Figure 3.9).

Auger Lineshape Evolution, Part 1

Co/Oxide/Si(111)

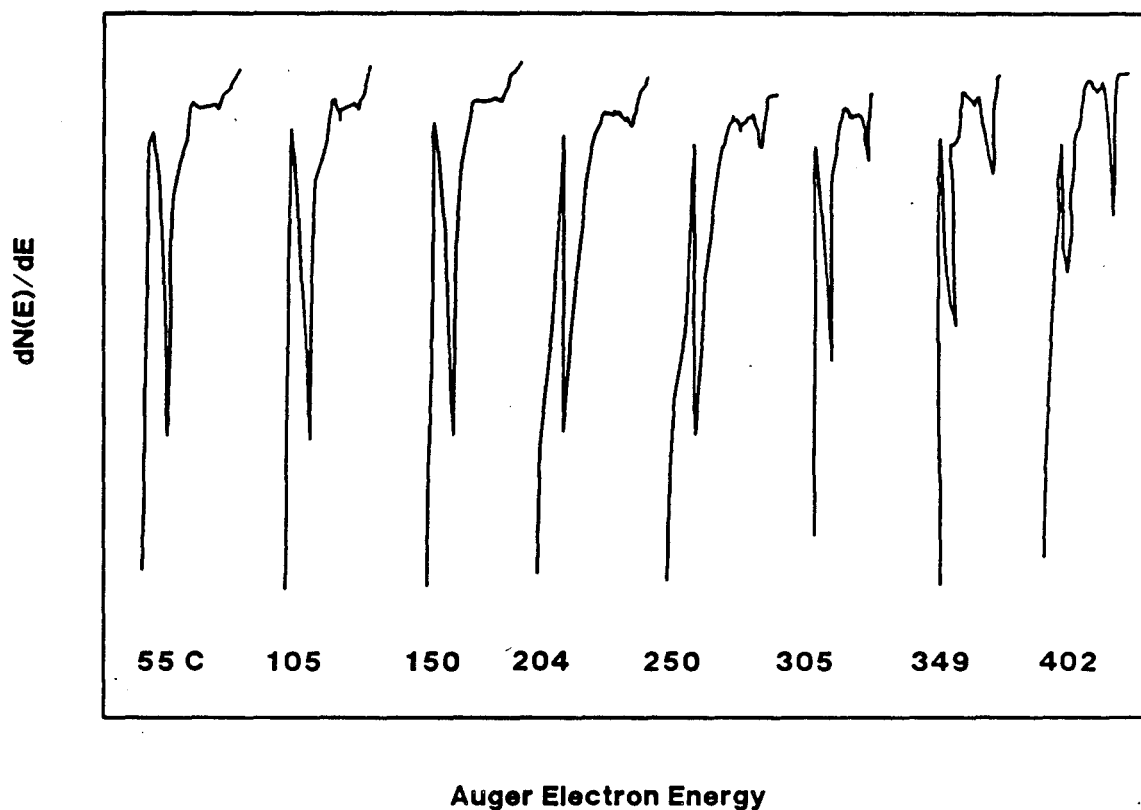


Figure 3.11.A. The change in the Co and Si Auger lineshapes during the reaction of Co with an oxidized Si substrate (Part 1). Temperatures ($^{\circ}\text{C}$) at which spectra were taken are indicated.

Auger Lineshape Evolution, Part 2

Co/Oxide/Si(111)

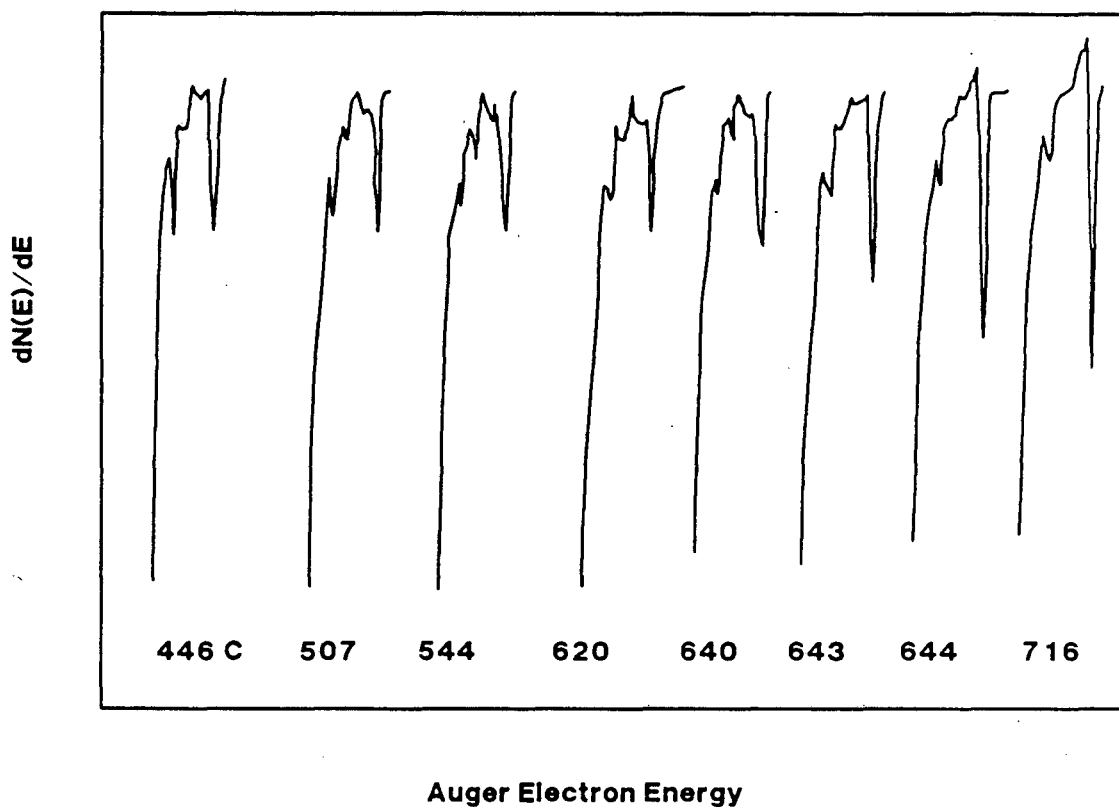


Figure 3.11.B. The change in the Co and Si Auger lineshapes during the reaction of Co with an oxidized Si substrate (Part 2). The oxidized shape of the Si peak disappears at about 650°C.

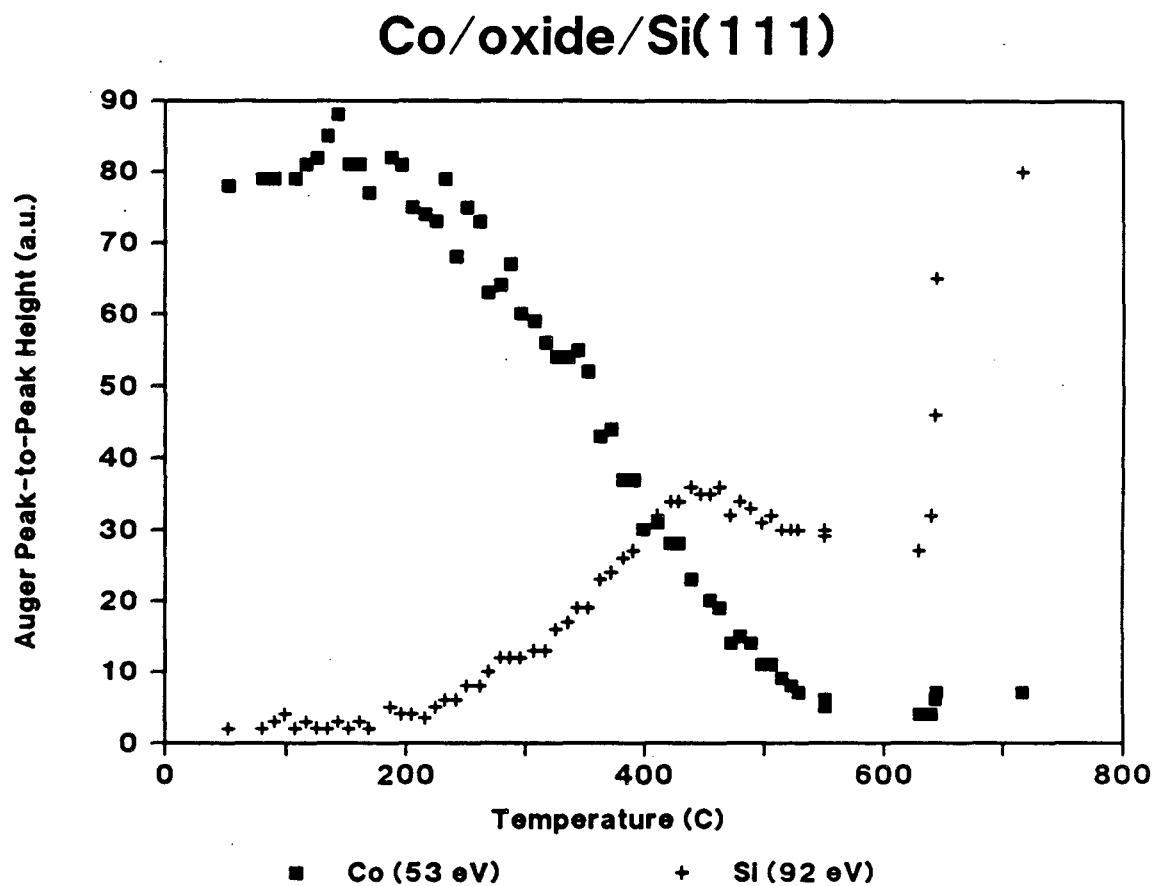


Figure 3.12. The change in the composition of the near-surface region as Co reacts with oxidized Si. Both the Co and the Si peak-to-peak heights increase after 650°C, the temperature at which the surface silicon oxide disappears (Figure 3.11).

Final AES of Co/ox/Si(111)

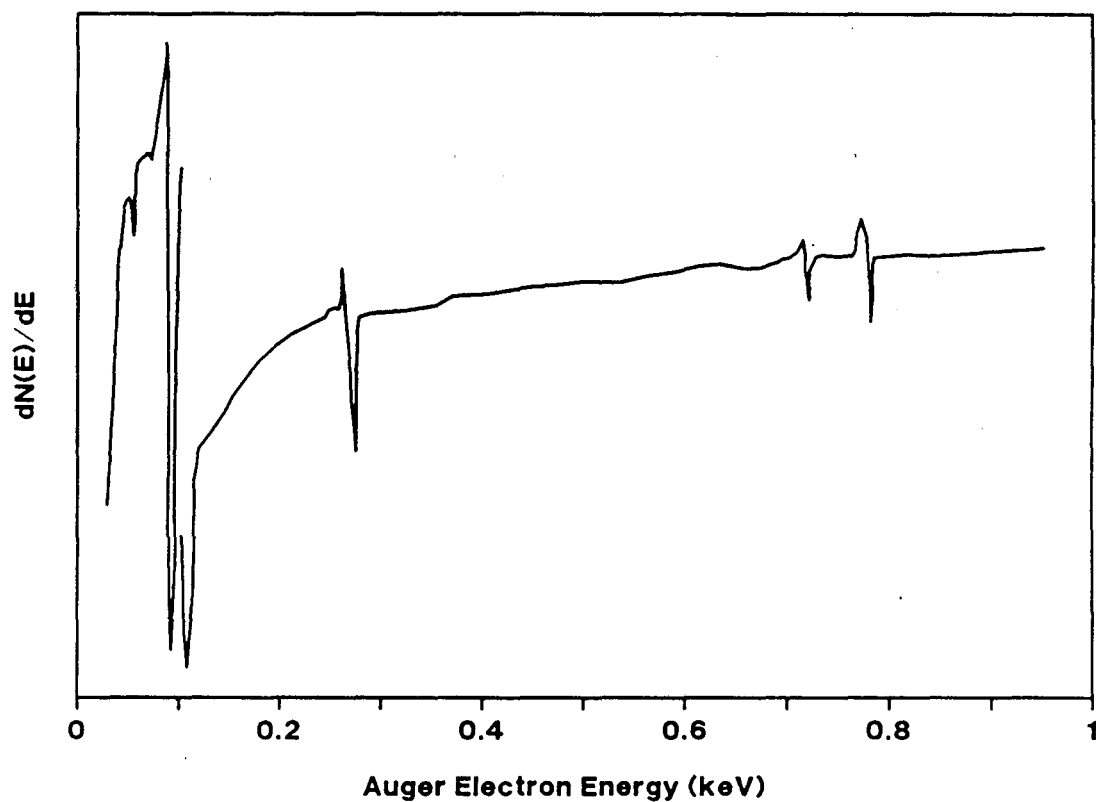


Figure 3.13. The final Auger spectrum after the reaction of Co with oxidized Si(111). This surface contains a 7×7 surface reconstruction, as determined by LEED.

AES of Thin Nitride on Si(111)

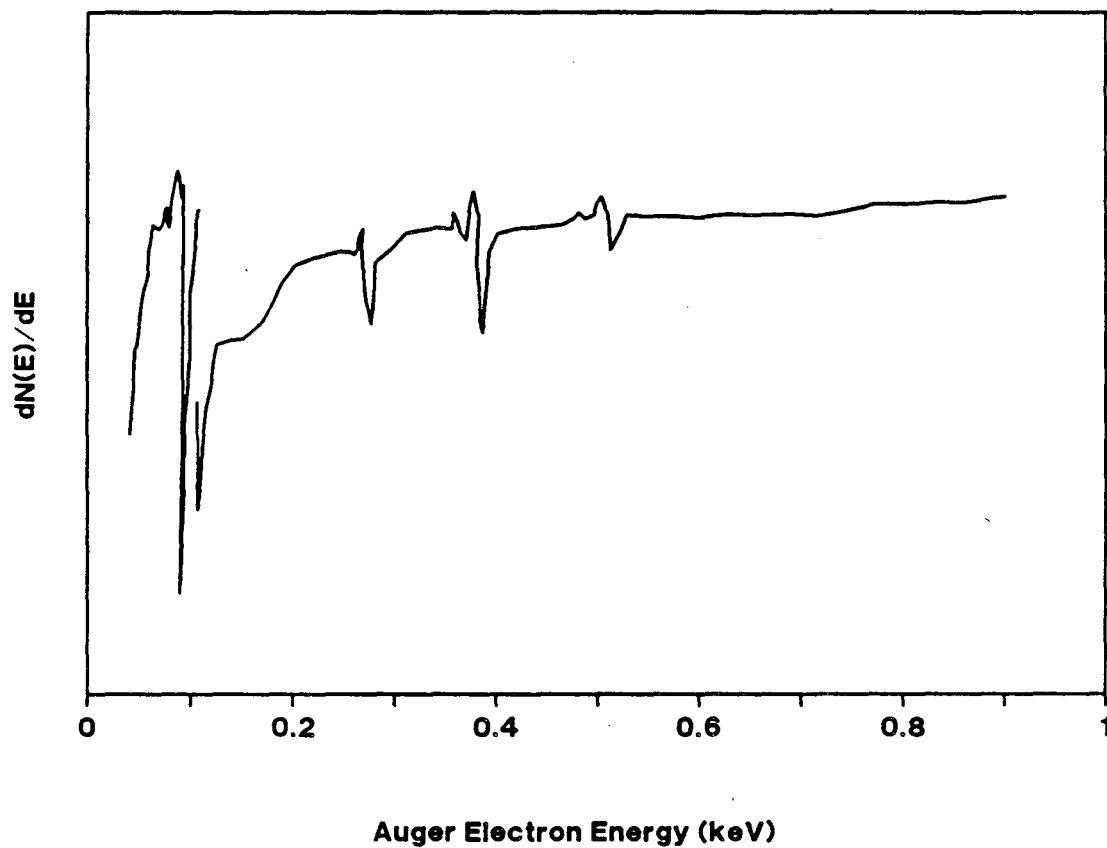


Figure 3.14. The Auger spectrum of a thin nitride layer on Si(111), showing N (384 eV) as well as C (273 eV) and O (512 eV).

AES of Thin Nitride on Si(111) After Annealing

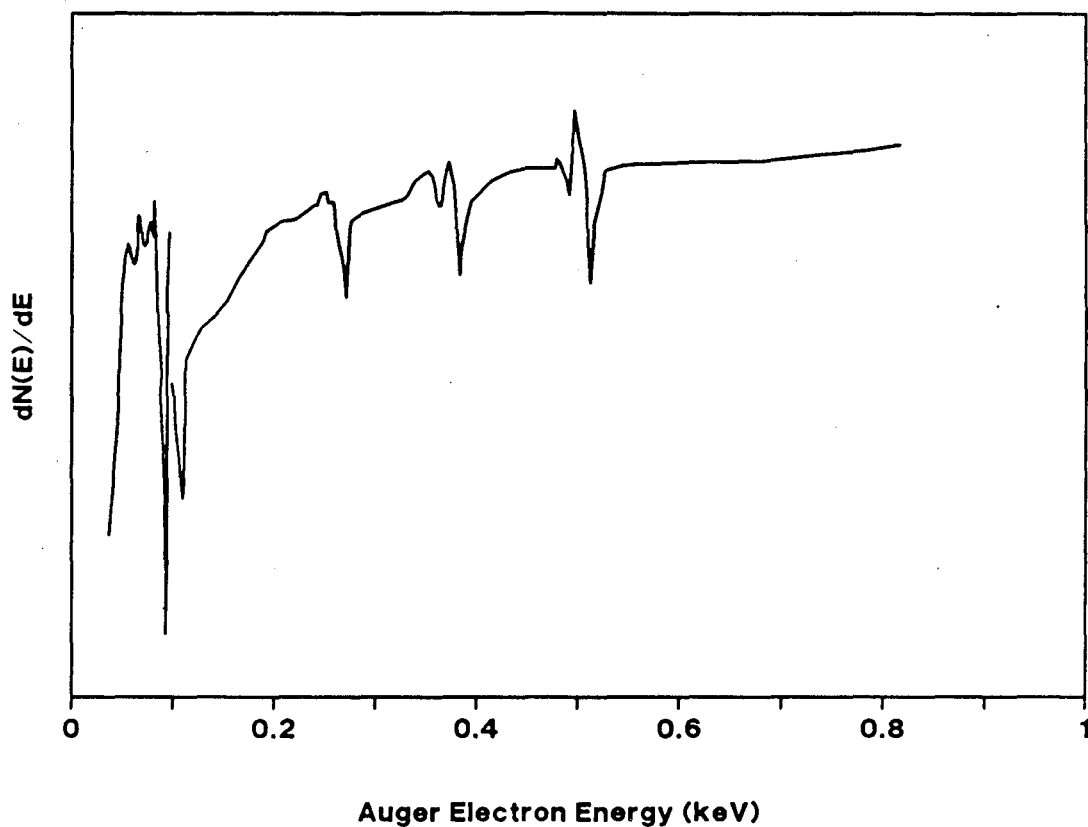


Figure 3.15. The nitrated surface of silicon, obtained after heating to 900°C.

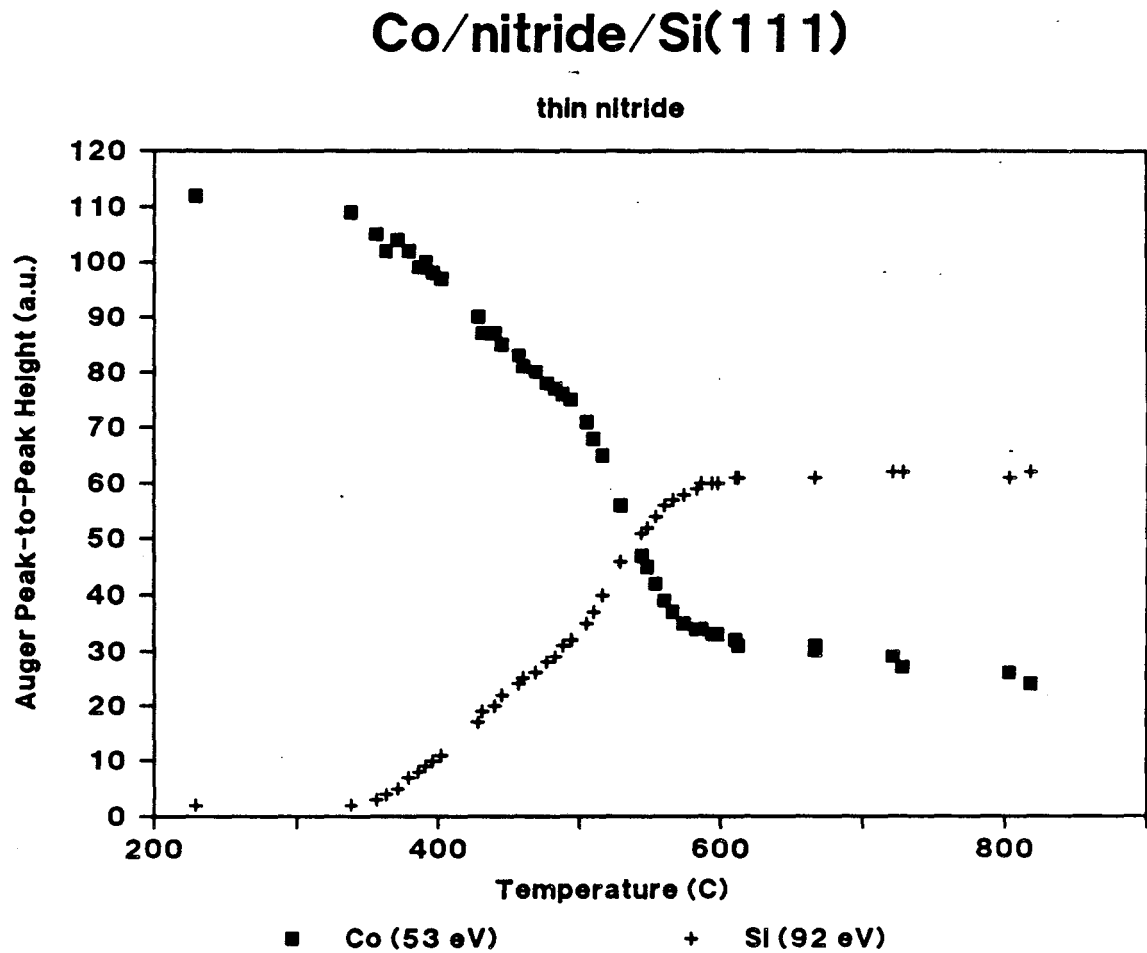


Figure 3.16. The change in the Co and Si concentrations near the sample surface as a function of temperature for the reaction of Co with a nitrided Si(111) substrate.

Thick Nitride on Si(111)

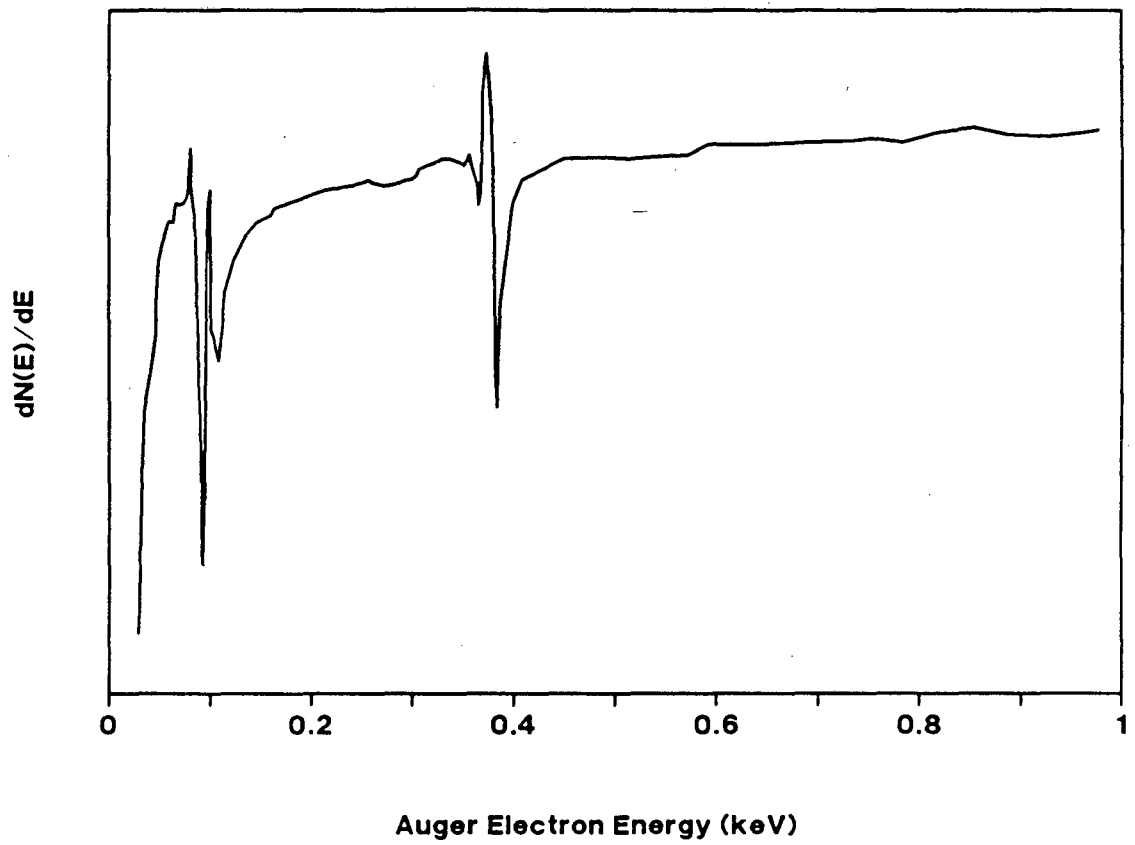


Figure 3.17. The Auger spectrum of a thicker surface nitride on Si(111), obtained by improving the aim of the nitrogen ion beam.

AES of Thick Nitride on Si(111) After Annealing

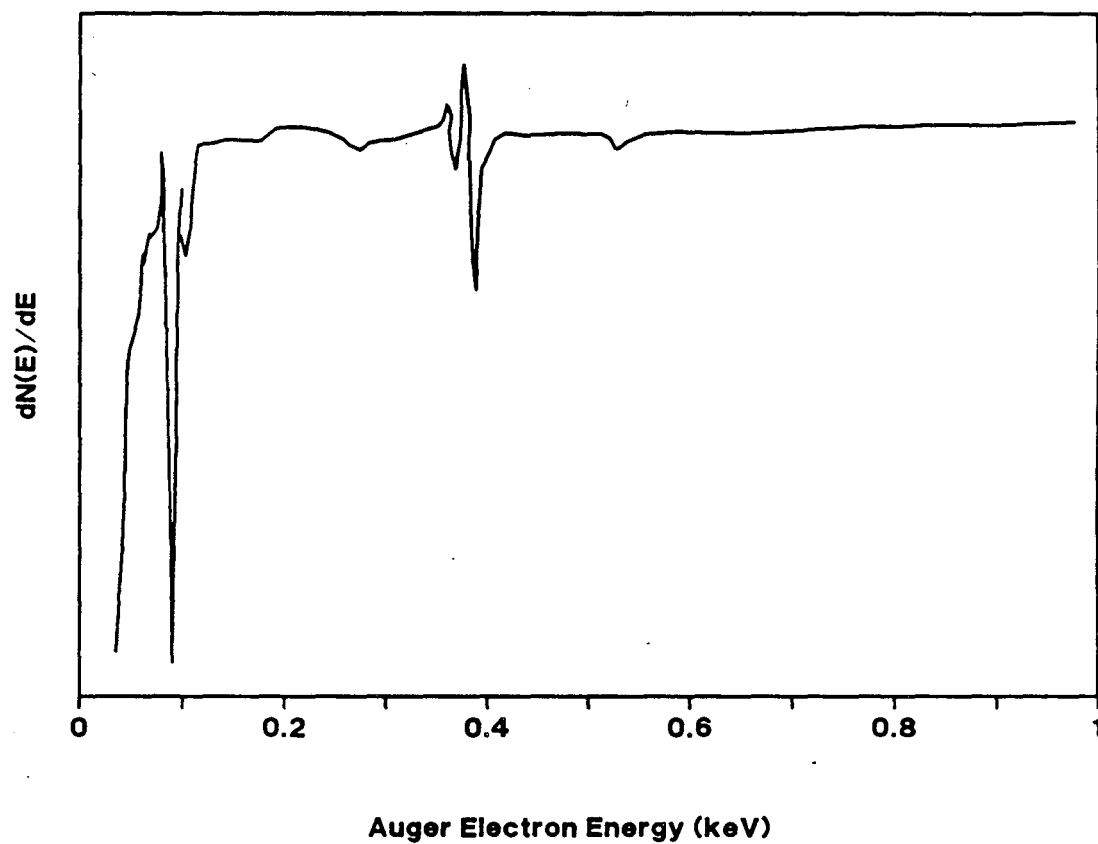


Figure 3.18. The Auger spectrum of the thicker nitride surface after annealing at 750°C.

AES of Thick Nitride on Si(111)

30-100 eV

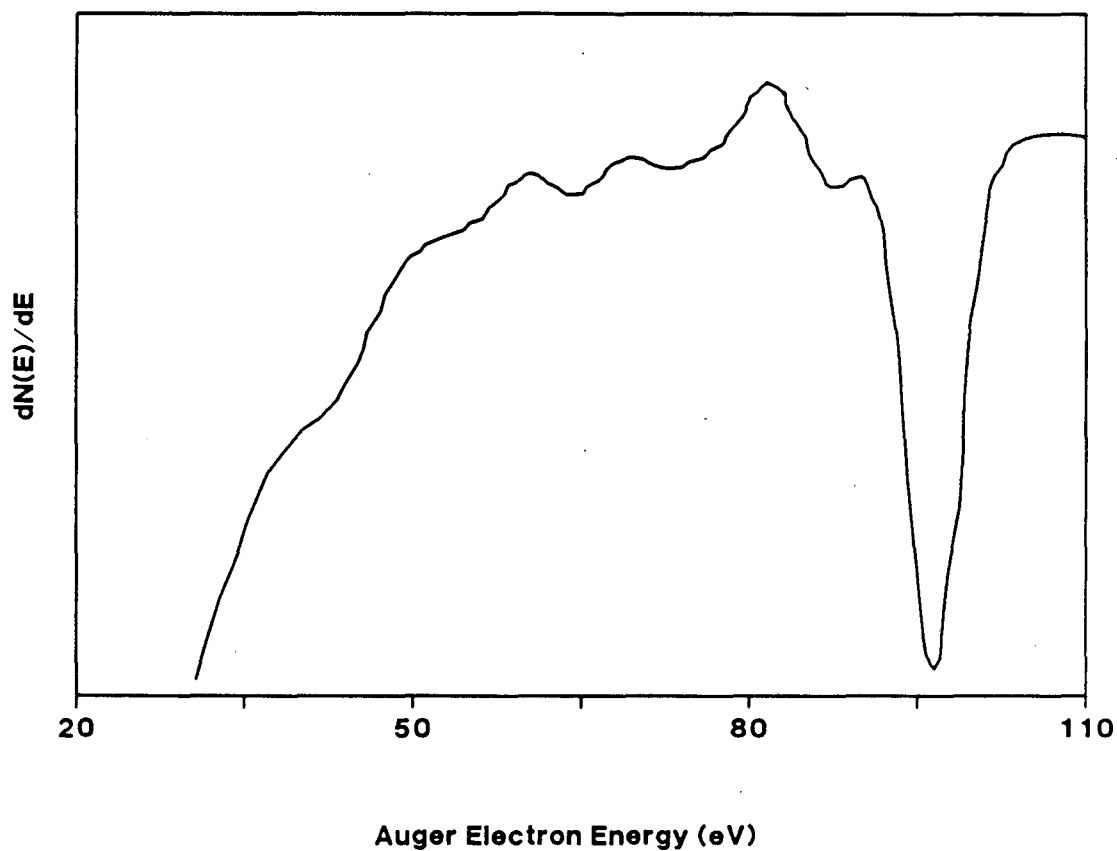


Figure 3.19. The expanded Auger spectrum of the surface nitride, showing the nitrified lineshape of the Si peak.

Co on Thick Nitride Layer

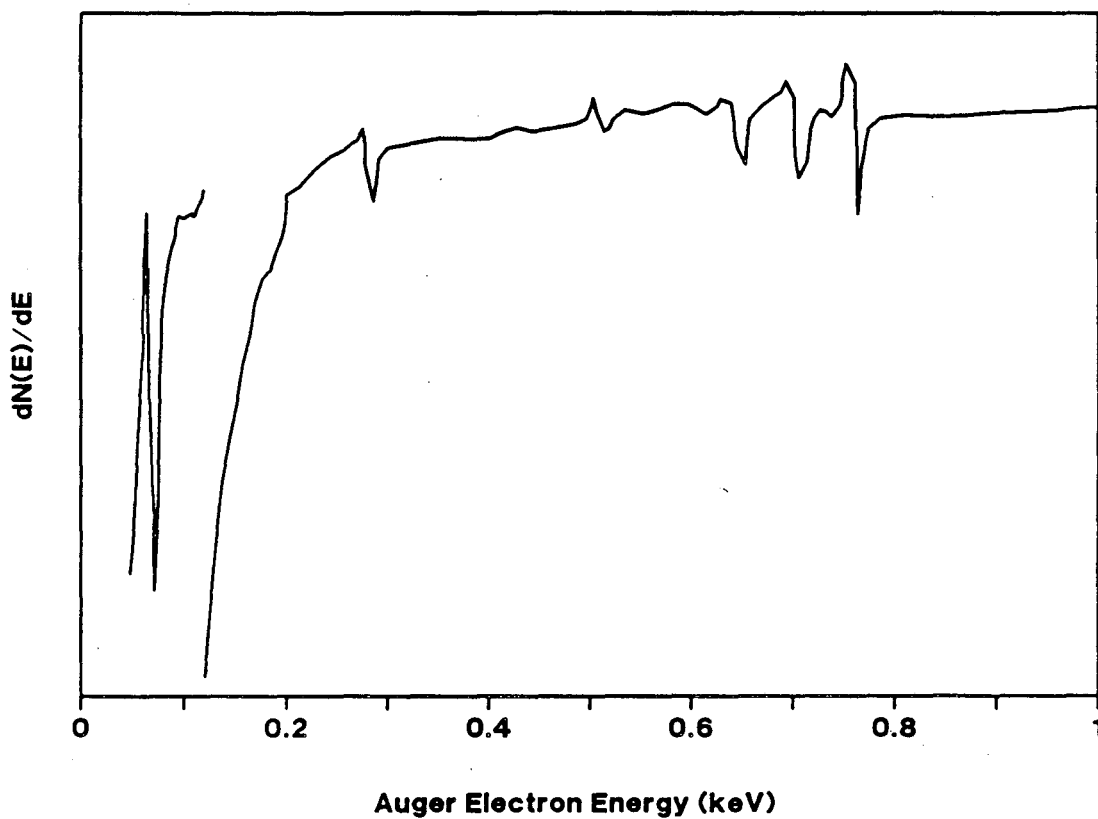


Figure 3.20. The Auger spectrum of 30 Å of Co deposited on the thicker surface nitride.

Evolution of AES, Co/N/Si(111)

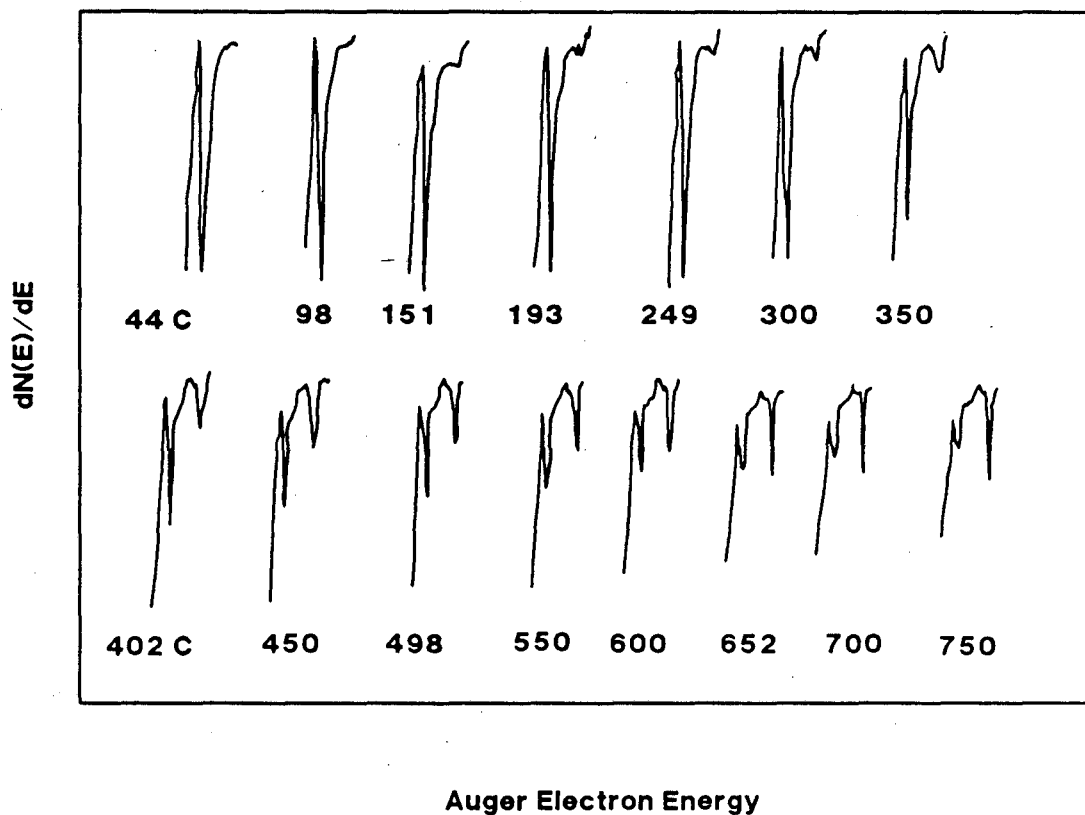


Figure 3.21. The evolution of the Co and Si peak shapes during the reaction between Co and nitrided Si at increasing temperatures.

Co/nitride/Si(111)

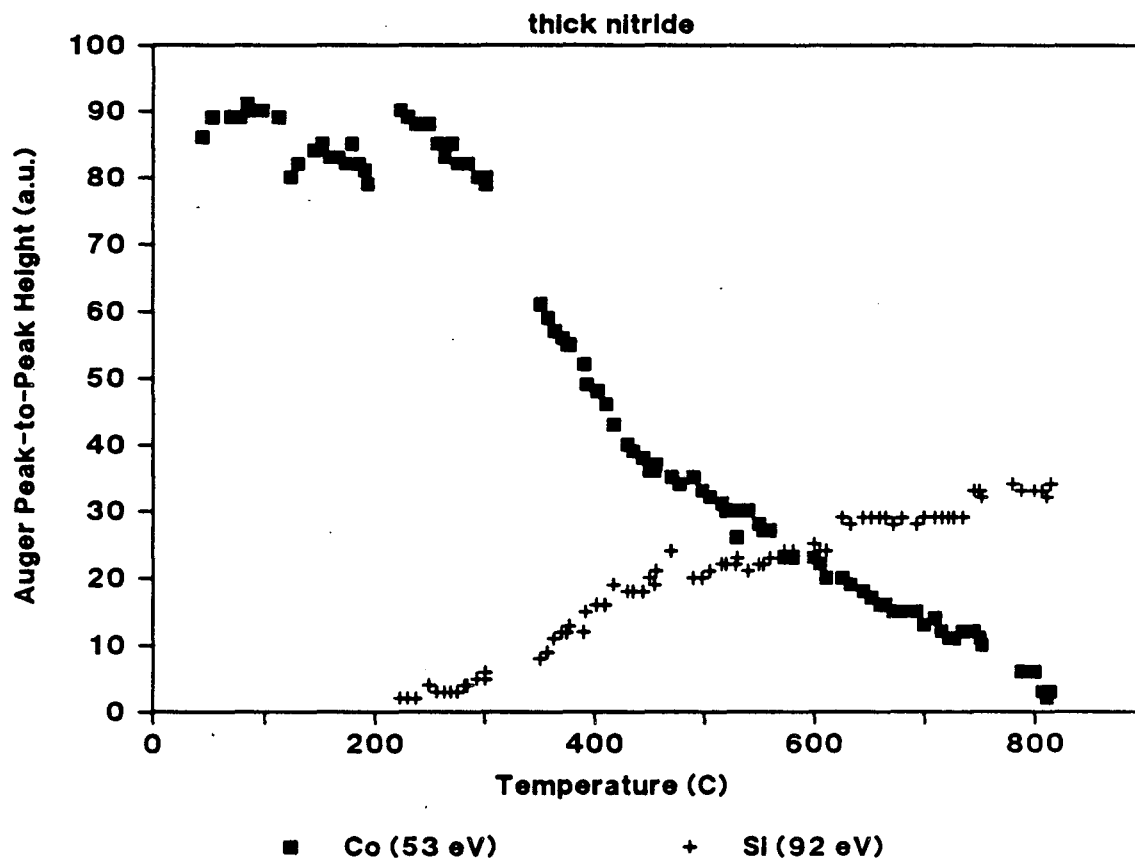


Figure 3.22. The change in Co and Si peak-to-peak heights as a function of temperature, showing the evolution of the composition of the near-surface region.

Final AES after Annealing

Co/nitride/Si(111)

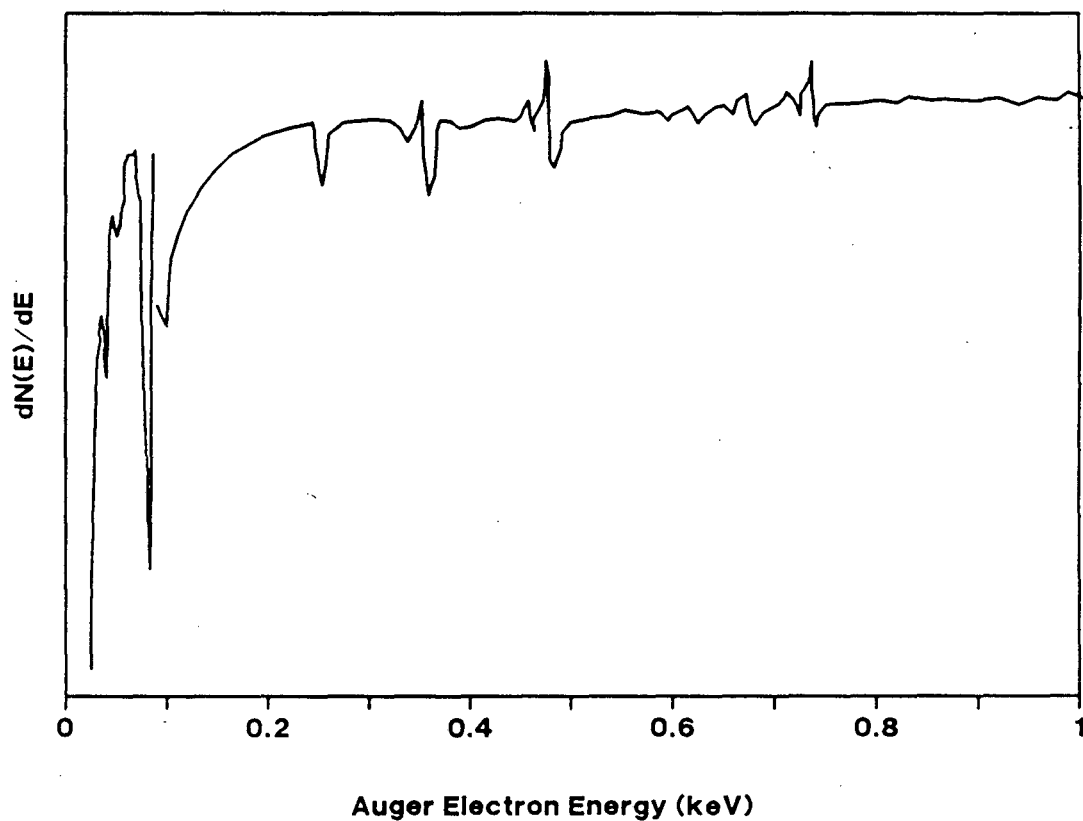


Figure 3.23. The final Auger spectrum after heating to 750°C, indicating the presence of Co and nitrided Si.

AES of Final Silicide

30-100 eV

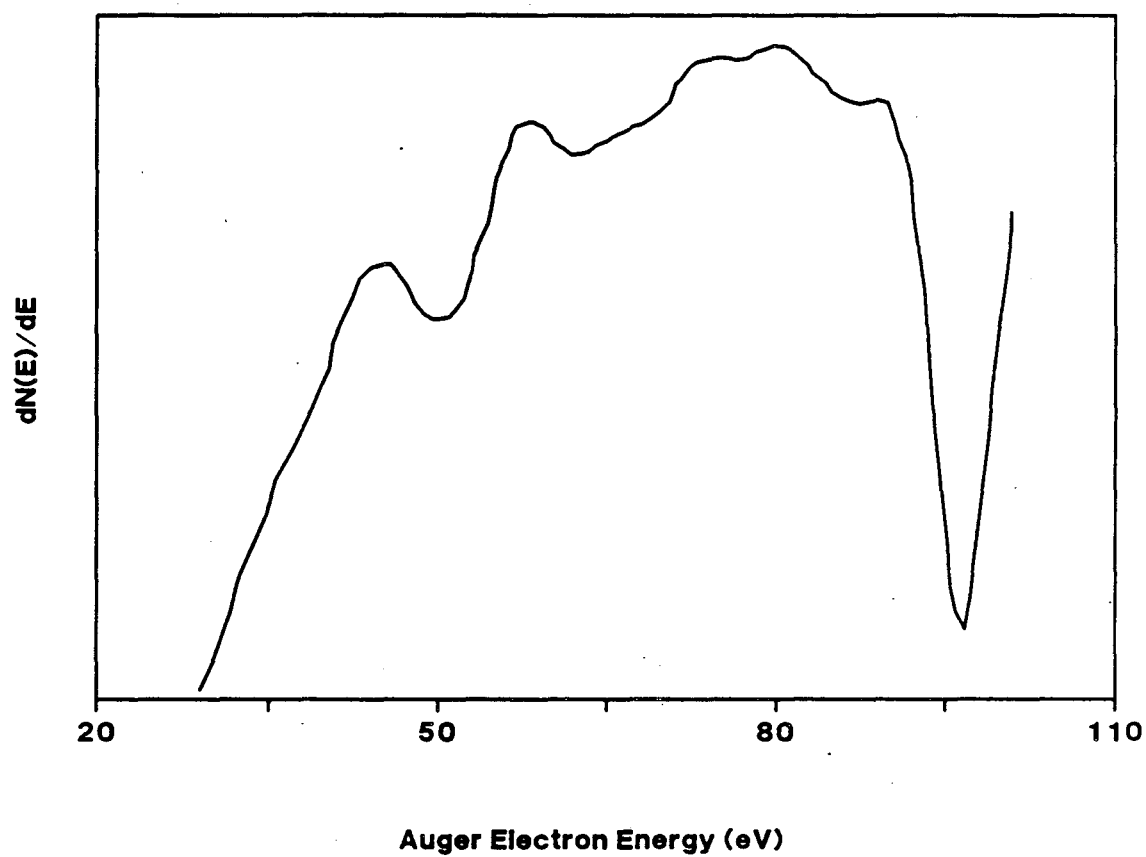


Figure 3.24. The expanded Auger spectrum showing the nitrided shape of the Si peak.

4. THE SURFACE CHEMISTRY OF CoSi_2

4.1. INTRODUCTION

CoSi_2 is an important material for electrical contacts to Si wafers because of its excellent epitaxial quality on Si(111) and low resistivity, as discussed in the Chapter 3. The reactivity of CoSi_2 surfaces is an important consideration in the commercial use of this material. This Chapter explores the surface properties of this important material, focusing on the surface structure and chemistry. The surfaces of epitaxial films, like those of single crystals, may be studied to characterize the properties and structures of specific crystallographic orientations. The surface of CoSi_2 , like that of any material, determines many of the properties of the material, such as its resistance to chemical or physical attack, since the surface is where such reactions occur.

One of the primary motivations in the study of CoSi_2 is the possibility of epitaxial growth of Si films over $\text{CoSi}_2/\text{Si}(111)$ to form novel electronic devices such as the metal base transistor.^{1,2,3,4} Since epitaxial Si growth takes place on the CoSi_2 film, the CoSi_2 surface is of vital importance in determining the properties of the final Si film. In addition, the structure and chemistry of the newly formed Si/ CoSi_2 interface determine the electrical properties of the resulting metal-semiconductor junction. The enrichment of the CoSi_2 surface in Si caused by heating past the CoSi_2 formation temperature (450-500°C),

observed in Chapter 3, represents the first stages of such Si growth on CoSi_2 . The study of thin epitaxial layers of Si on CoSi_2 , whether from overannealing or silicon deposition, may yield insights into Schottky barrier formation, similar to information gained from studies of the initial interaction of metal films with Si substrates.

The shape of the Si Auger peak observed during the reaction between Co and oxidized Si(111) in Chapter 3 demonstrates the existence of a surface oxide after Co has diffused into the underlying Si. The disappearance of this oxide with further heating, presumably by SiO sublimation, suggests a novel route to the removal of excess surface Si from CoSi_2 by first oxidizing the Si-rich CoSi_2 film and heating until SiO sublimation occurs. The oxidation of silicide surfaces is of importance in the construction of multilevel devices, which depend on oxides to electrically isolate different features from each other.

The surface chemistry of $\text{CoSi}_2(111)$ was studied with temperature programmed desorption (TPD), using benzene as a probe molecule. TPD experiments are used to determine the activation energy of desorption (E_a), which gives information about the strength of adsorbate-surface interaction. Benzene molecules bond to transition metal surfaces by donating electron density from the π ring of benzene to the surface and adsorb with the plane of the ring parallel to the surface.⁵ The strength of the benzene-surface bond gives information about the extent of the benzene π electron donation to the surface. Benzene TPD experiments also serve to compare the surface of

$\text{CoSi}_2(111)$ to the surfaces of $\text{Si}(111)$ and $\text{NiSi}_2(111)$. The absence of benzene decomposition on these surfaces facilitates experimentation, as sputter cleaning the surface of such a thin silicide film is difficult or impossible. Instead, clean silicide surfaces need to be prepared by completely sputtering away the silicide, depositing a fresh metal film, and annealing to form a new silicide layer.

4.2. RESULTS

4.2.1. $\text{CoSi}_2(111)$ (1×1) Formation

Epitaxial CoSi_2 layers were prepared on silicon by first evaporating cobalt on an atomically clean $\text{Si}(111)$ 7×7 silicon substrate, followed by annealing at 500°C . The LEED pattern (not shown here) of the silicide formed in this manner is 1×1 . The Auger spectrum of such a silicide film is given in Figure 4.1, showing Co peaks at 53, 656, 716, and 775 eV together with a Si peak at 92 eV. The Si (92 eV) peak in CoSi_2 does not have the 72 eV peak of a clean Si surface.

During the reaction of a Co film with a clean $\text{Si}(111)$ substrate described in Chapter 3, a Si (LVV) lineshape was observed which closely resembled the Si peak shape found in this CoSi_2 (1×1) film, including the lack of a 72 eV peak. Figure 3.5 from Chapter 3 shows that the Si (LVV) lineshape contained no 72 eV peak below 420°C , but heating above 530°C

caused it to appear. The presence of this peak was also accompanied by an increase in the amount of Si versus Co detected AES, especially above 530°C. The final film had an Auger peak at 72 eV and a 7×7 reconstruction, indicating that further heating of CoSi_2 (1×1) films not only changes the composition of the near surface region, but also the surface order.

4.2.2. Oxidation of $\text{CoSi}_2(111)$ (7×7)

The reaction between Co and an oxidized Si(111) substrate at elevated temperatures eventually results in the presence of oxidized Si over a CoSi_2 film, as reported in Figure 3.11 of Chapter 3. With increasing temperature (640°C), however, this oxide begins to disappear, judging by the lineshape of the Si (LVV) Auger peak. An Auger spectrum taken after heating to 716°C shows no oxygen peak (512 eV) nor the characteristic oxidized shape of the Si (LVV) peak. The mechanism for the disappearance of the oxide is presumably SiO sublimation, as is observed from oxidized Si at 850-900°C.⁶

During the heating of this system, the Si (LVV) lineshape passes through a shape indicating not only the absence of oxide, but also the lack of the 72 eV peak characteristic of surface enrichment in Si. With further heating a Si-rich silicide phase was formed. The presence of an unenriched silicide phase after SiO sublimation suggests a route to the removal of excess surface Si by oxidizing the surface and subliming SiO.

To test this hypothesis, the surface of an overannealed, Si-rich (7×7) CoSi_2 surface was exposed to 1 atm. of O_2 for 3 min., the same oxygen exposure used to oxidize Si(111) in Chapter 3. The Auger spectrum of this oxidized surface appears in Figure 4.2, clearly showing both the O (512 eV) Auger peak. The shape and peak-to-peak height of the Si (LVV) Auger peak are very similar to those of an oxidized Si(111) surface (Chapter 3, Figure 3.9) and to the surface oxide that forms during the reaction between Co and an oxidized Si substrate. Heating to 740°C is sufficient to remove all traces of oxygen in the Auger spectrum. The spectrum at this temperature also indicates an unenriched CoSi_2 surface lacking a 72 eV peak. The next Auger spectrum at this temperature, however, contains the 72 eV peak of a Si-rich surface. LEED shows a 7×7 reconstruction, consistent with the new shape of the Si (LVV) Auger peak. This Si-enriched surface was re-oxidized and heated, but it was never possible to stop heating after SiO sublimation and before silicide reconstruction, and a Si-rich 7×7 silicide was always obtained.

4.2.3. Benzene TPD

The surface chemistry of CoSi_2 (1×1) was investigated by adsorbing benzene, followed by temperature programmed desorption (TPD). The strength of the bond between the adsorbed benzene and the CoSi_2 (1×1), gives information about the π bonding of benzene to the surface. This π bonding interaction is compared to the π bonding of benzene to the surfaces

of isomorphous NiSi_2 and to $\text{Si}(111)$.

The TPD trace of benzene adsorbed on $\text{Si}(111) 7 \times 7$ is shown in Figure 4.3. A low initial surface coverage of benzene results in only a single desorption peak at 195°C . As the surface coverage of benzene is increased, a second, lower temperature (100°C) peak grows in, which becomes much larger than the 195°C peak at higher benzene coverages. No thermal decomposition of benzene on $\text{Si}(111)$ is observed, as evidenced by the lack of H_2 desorption and the absence of any increase in surface carbon content by AES.

The thermal desorption of benzene from $\text{CoSi}_2(111) (1 \times 1)$ results in TPD traces that are very similar to those from $\text{Si}(111)$ (Figure 4.4), though much less desorption is observed. Two desorption peaks (75°C and 175°C) are again observed, though at slightly lower temperatures than in the case of benzene desorption from $\text{Si}(111)$. Only benzene desorption at 175°C is found for low coverages, and higher doses fill in the bigger, lower temperature peak. Again, no benzene decomposition is observed.

The TPD traces for benzene desorption from $\text{NiSi}_2(111)$ obtained by Klarup are shown in Figure 4.5.⁷ The shapes of the desorption peaks are again similar to those from $\text{CoSi}_2(111)$ and $\text{Si}(111)$ described above, displaying the dominance of the high temperature peak only at low coverages and the lack of benzene decomposition. The trend to lower benzene desorption temperatures from $\text{Si}(111)$ to $\text{CoSi}_2(111)$ is also repeated here, as desorption peaks from NiSi_2 occur at 82 and 150°C .

4.3. DISCUSSION

4.3.1. $\text{CoSi}_2(111)$ (1×1) Formation

The reaction between Co and Si(111) described in Chapter 3 produced an epitaxial CoSi_2 film displaying a 7×7 surface reconstruction and a 72 eV peak in the Si (LVV) lineshape. Here, it was found that by limiting the reaction temperature to 500°C, CoSi_2 films having unreconstructed (1×1) surfaces were obtained which lacked the 72 eV peak of reconstructed, Si-rich silicide surfaces. A surface having the same Si (LVV) lineshape was observed during the reaction between Co and Si in Chapter 3, and it was found that increasing the temperature further causes the amount of Si in the near surface region to increase, as detected by AES. This increase in Si was accompanied by the appearance of a 72 eV peak and the formation of a 7×7 reconstruction.

Similar 1×1 CoSi_2 surfaces have been obtained by a number of researchers. D'Avitaya and coworkers reported that reactions between a 33 Å film of Co and Si(111) produced an unreconstructed film below 750°C.⁸ A 7×7 reconstruction was observed for thick (>100 Å) CoSi_2 films or CoSi_2 films formed at temperatures above 750°C. Unreconstructed films were formed at temperatures up to 720°C for initial Co thicknesses below 40 Å. Thicker unreconstructed films were found only at formation temperatures of

650°C or lower. D'Avitaya also used scanning electron microscopy (SEM) to reveal the existence of CoSi_2 islands on a bare Si substrate for films showing a 7×7 reconstruction. SEM was used by other groups to observe the existence of epitaxial CoSi_2 islands on a bare Si substrate formed by annealing a 300 Å Co film at 600-900°C⁹ and by molecular beam epitaxy (co-deposition of Co and Si on a hot Si(111) substrate) above 650°C.¹⁰

D'Avitaya has explained the 7×7 LEED pattern observed during overannealing as the characteristic 7×7 LEED pattern of a clean Si(111) substrate superimposed on a 1×1 CoSi_2 pattern. These results are contradicted by the LEED analysis of Wu et. al., which compared the intensities of the experimentally observed diffracted beams to calculated values for CoSi_2 surfaces formed above 600°C.¹¹ CoSi_2 films were observed by this technique, as were silicide films attributed to pre- and post-silicide phases. Heating at 900-1000°C resulted in a decrease in the near-surface Co concentration and a 7×7 reconstruction, which was attributed to a post-silicide phase and not to a bare Si(111) 7×7 substrate. Either the formation of a Si-rich "post-silicide phase" or the presence of CoSi_2 islands on a bare Si(111) substrate would account for the increase in the Si detected by AES and the 7×7 surface reconstruction observed in Chapter 3.

4.3.2. Oxidation of $\text{CoSi}_2(111)$ (7×7)

The reaction between Co and an oxidized Si(111) substrate described in Chapter 3 results in the sublimation of SiO above 640°C. The sublimation of SiO produces a Si (LVV) Auger lineshape lacking the 72 eV peak associated with surface reconstruction and Si enrichment. Further heating of this unenriched CoSi₂ surface causes the Si enrichment to reappear, accompanied by a 72 eV Auger peak and a 7 × 7 surface reconstruction. The lineshape of the Si (LVV) Auger peak obtained after Co has diffused into the bulk indicates the presence of a surface oxide layer and is consistent with a SiO_x/CoSi₂/Si structure. The presence of this surface oxide suggests a route to the removal of excess surface Si by oxidizing a reconstructed, Si-rich CoSi₂ surface and removing Si through the subliming of SiO.

Such a route to an unreconstructed CoSi₂ surface suggests the oxidation of the surface of a Si-rich CoSi₂ film followed by SiO sublimation. As Si has a much larger heat of oxidation than Co, it would be expected that only Si oxidizes, and not Co. The shape of the Si (LVV) peak in the Auger spectrum obtained after the oxidation of a Si-rich CoSi₂ surface indicates that this is the case. The full Auger spectrum of this oxidized surface closely resembles the spectrum of the surface oxide observed during the reaction between Co and the oxidized Si substrate, supporting the existence of a SiO_x/CoSi₂/Si structure.

Heating the oxidized CoSi₂ sample to 700°C was sufficient to remove the surface oxide and produce a Si(LVV) lineshape characteristic of a 1 × 1 CoSi₂ surface by the absence of a peak at 72 eV. Unfortunately, the anneal

could not be stopped before the formation of a Si-rich, 7×7 surface. This result is consistent with the higher temperature necessary for SiO sublimation than for CoSi_2 reconstruction. Perhaps it is still possible to stop the anneal after SiO sublimation and before surface reconstruction: while it was not possible to do so in these experiments, the unreconstructed surface did exist for the 30 sec. required to record the Auger spectrum.

It is interesting that the temperature of sublimation from CoSi_2 is over 150°C lower than the temperature of sublimation from Si. In addition, the unreconstructed CoSi_2 surface detected by AES after oxidation and sublimation has to cover the Si substrate, since the 72 eV peak of clean Si was not observed in the Si(LVV) lineshape. If the reconstructed, Si-rich CoSi_2 surface does indeed consist of CoSi_2 islands observed by the researchers mentioned previously, then the oxidation or sublimation must reform the silicide film and cause it to cover the substrate.

The oxidation of $\text{CoSi}_2(100)$, has been studied by Castro and coworkers, who found that oxygen only bonds to Si, leaving the Co unoxidized.¹² In addition, oxygen uptake was ten times faster on $\text{CoSi}_2(100)$ than on Si(111), though 200 times slower than on Co metal. From the oxidation results it was concluded that the top layer of $\text{CoSi}_2(100)$ consists of Si atoms. Similar results were obtained for the oxidation of NiSi_2 films, where no Ni oxidation was observed and the increased oxidation rate of NiSi_2 versus Si was explained by the dissociation of O_2 by Ni atoms.¹³ The Si of the oxide formed on NiSi_2 was shown to be less oxidized than Si in SiO_2 . By

extension, the thin oxide formed on CoSi_2 may also contain Si that is not oxidized all the way to SiO_2 .

The formation of thick SiO_2 films on CoSi_2 by O_2 ¹⁴ and steam¹⁵ oxidation has been explored as well. The oxidation of CoSi_2 is faster than that of Si, with SiO_2 growth occurring through the diffusion of oxygen to the oxide/silicide interface. There is disagreement on the mechanism of oxide film growth based on whether the supply of Si to be oxidized comes from the Si substrate, or whether it originates from the top layer of silicide and is accompanied by Co migration to the Si/ CoSi_2 interface, where CoSi_2 is then formed.

4.3.3. Benzene TPD

The thermal desorption of benzene adsorbed on $\text{CoSi}_2(111)$ give information about the strength of the π bonding between the adsorbate and substrate, and provide insight into the surface chemistry of CoSi_2 . The TPD results of benzene desorption from $\text{Si}(111)$, $\text{CoSi}_2(111)$, and $\text{NiSi}_2(111)$ underscore the similarities between these surfaces, as does the lack of any benzene decomposition. The only effect of Co (and Ni) seems to be a slight lowering of the desorption temperatures of benzene on these silicides compared to silicon.

The striking similarities in the TPD results of benzene from CoSi_2 and Si strongly suggest that the top layer of CoSi_2 consists of Si atoms, as does

NiSi₂(111).¹⁶ The arrangement of Co and Si in an ideal, unreconstructed CoSi₂(111) surface terminating with a single Si layer is shown in Figure 4.6, together with an ideal Si(111) surface. A comparison of these two (unreconstructed) surfaces reveals that the hexagonal arrangement and Si-Si spacing of top layer Si atoms is identical to within the 1.2% lattice difference between CoSi₂ and Si. A benzene molecule, then, adsorbs on an essentially identical Si-terminated layer in both CoSi₂ and Si. This identical surface Si geometry explains the close similarity between the CoSi₂ and Si benzene TPD results.

The only difference in the CoSi₂ and Si TPD results is the temperature of the maximum rate of desorption. Since the surfaces have the same structure and Si composition, the difference must be attributed to the presence of cobalt. In the case of benzene adsorption on NiSi₂, the donation of electron density from Ni to Si, observed by Cheung et. al.,¹⁷ has been invoked to account for the decreased peak desorption temperatures from NiSi₂ compared to Si.⁷ A similar electron density donation from Co to Si could also explain the lower desorption temperatures observed for benzene from CoSi₂, though only minimal charge transfer between Co and Si has been detected by XPS.¹⁸ Since adsorption of benzene seems to take place by π electron transfer from the benzene ring to the Si-terminated surface, any increase in Si electron density at the expense of Co will decrease the degree of π electron density donated by benzene.

The surface termination of CoSi_2 in a single Si layer is not the only explanation for the observed TPD results. The CoSi_2 could terminate in two or more Si layers without changing the surface geometry. At this point the surface cannot be considered " CoSi_2 -like" anymore, yet two Si layers cannot constitute a separate Si phase. This calls into question the nature of a single topmost silicon layer, and underscores the similarity of TPD results between silicides and silicon.

The presence of multiple layers of Si on CoSi_2 has indeed been observed by many researchers, who have reported the existence of both 2^{19,20} and 3^{21,22} layers of Si over the topmost Co layer. The evidence favors the existence of 3 layers, which are said to consist of a Si(111) bilayer over a Si-terminating CoSi_2 film.

As the possibility of multiple Si layers over the CoSi_2 bulk seems likely, it would be interesting to study the effect of additional layers on the desorption temperature of benzene. Such an experiment might distinguish the reactivity of Si atoms in CoSi_2 and Si. In addition, the presence of multiple Si overlayers on CoSi_2 would eventually form a bulk-like Si overlayer. Since TPD seems to be sensitive to the electronic state of the top layer Si atoms, this might be a way to study the initial formation of a metal-semiconductor contact. (It would seem such a study is simpler than a study of a metal silicide produced by the deposition of a metal on silicon.) The band-bending resulting from M-Si contacts might also be studied by TPD as a function of silicon thickness. Here, the ability of benzene to donate to silicon atoms

might depend on the band energy. Such a study is not possible for metal overlayers on silicon because the high density of charge carriers of a metal confines the band bending to an extremely thin region.

4.4. CONCLUSIONS

Unreconstructed CoSi_2 films having a 1×1 LEED pattern can be grown on clean $\text{Si}(111)$ substrates in ultra-high vacuum by depositing Co and annealing at 500°C . Further heating results in the enrichment of the near surface region in Si and a 7×7 surface reconstruction, as observed in Chapter 3.

Exposing an overannealed CoSi_2 7×7 surface to O_2 causes Si to be oxidized, as verified by AES lineshape analysis. Above 700°C this oxide disappears, the most likely mechanism being the sublimation of SiO . Oxidation of an Si-rich CoSi_2 surface followed by SiO sublimation can be used to remove excess surface Si, and a lineshape of the Si (LVV) Auger peak corresponding to an unreconstructed CoSi_2 surface is observed. Unfortunately, the temperature at which SiO sublimation occurs is sufficient to cause the migration of Si to the surface, forming another Si-rich CoSi_2 surface.

Benzene TPD results on $\text{CoSi}_2(111)$ and $\text{Si}(111)$ surfaces (and previous results on $\text{NiSi}_2(111)$) are qualitatively very similar, though less adsorption and lower desorption temperatures are observed on the silicide surfaces. The

similarities suggest that the CoSi_2 layer terminates in at least one Si layer, which has the same geometry as top layer Si in (unreconstructed) Si(111). The lower desorption temperatures (E_a 's) of benzene from silicide surfaces are attributed to the donation of electron density from Co to Si, decreasing the ability of the benzene π ring to bond to the surface.

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AES of Unreconstructed CoSi₂(1 1 1) Surface

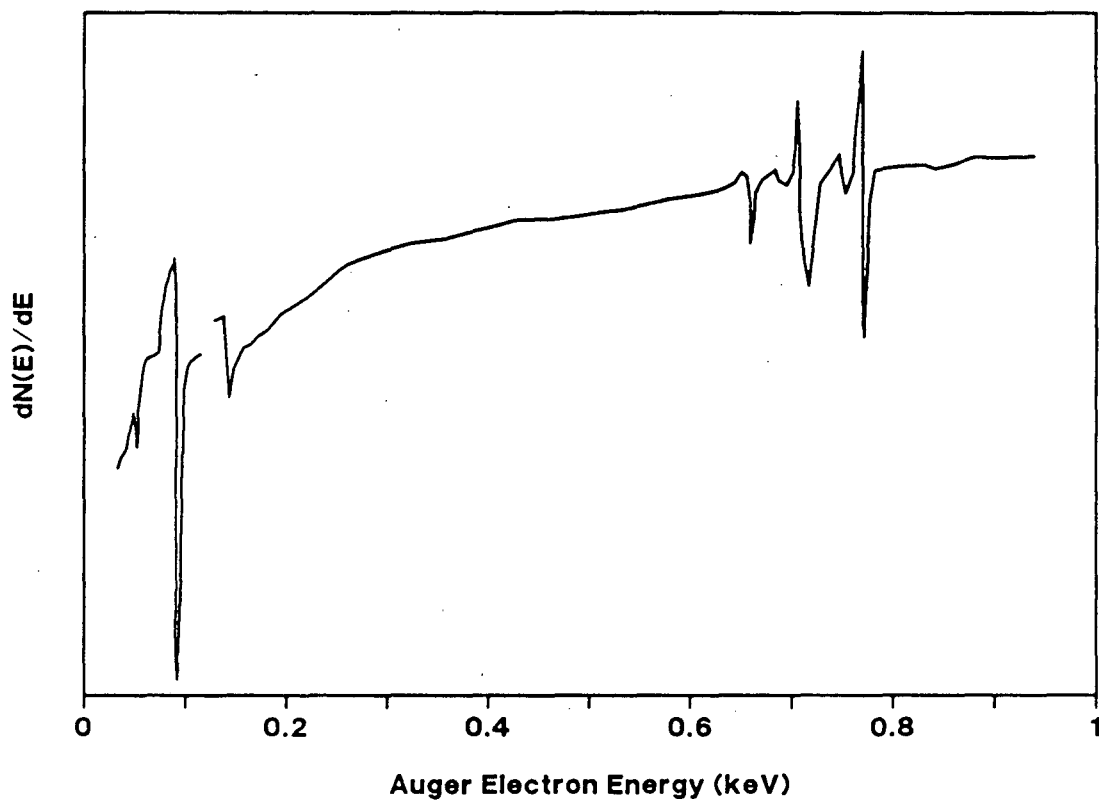


Figure 4.1. The Auger spectrum of an unreconstructed (1 × 1) CoSi₂ surface.

AES of Oxidized CoSi₂(111)

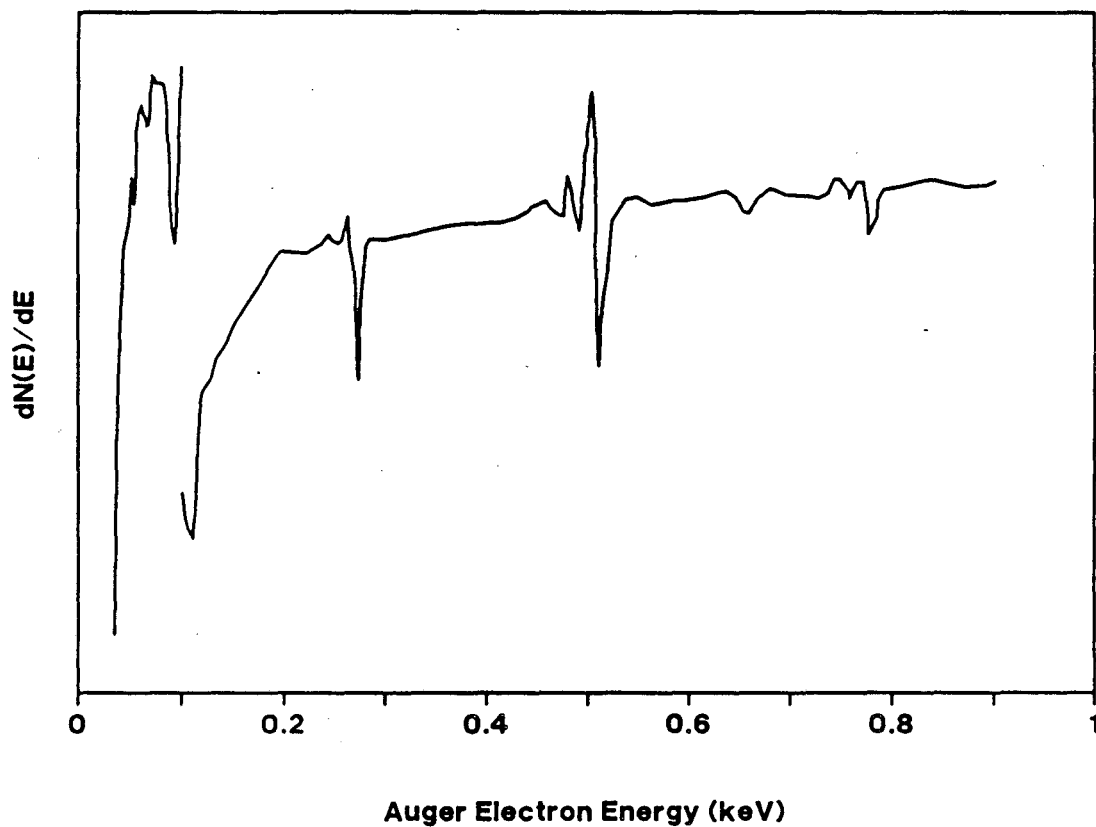


Figure 4.2. The Auger spectrum of an oxidized CoSi₂ surface. The Si (LVV) lineshape displays the same oxidized features as does the Auger spectrum of oxidized Si(111) (Figure 3.9 of Chapter 3). This spectrum closely resembles that of the surface oxide obtained during the reaction between Co and an oxidized Si substrate (Figure 3.11 of Chapter 3).

Benzene TPD on Si(111)

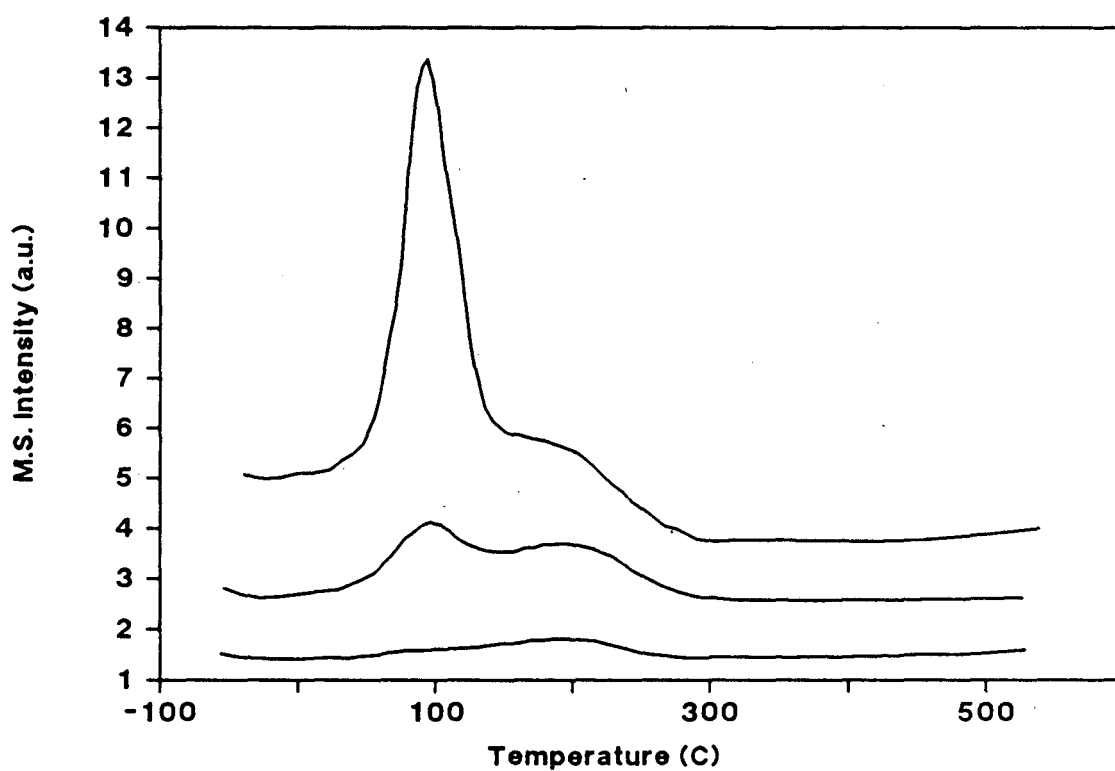


Figure 4.3. Benzene TPD traces from Si(111). Only a small, 195°C desorption peak is found for low initial benzene surface coverages. With increasing coverage, the larger 100°C peak grows in.

Benzene TPD on $\text{CoSi}_2(111)$

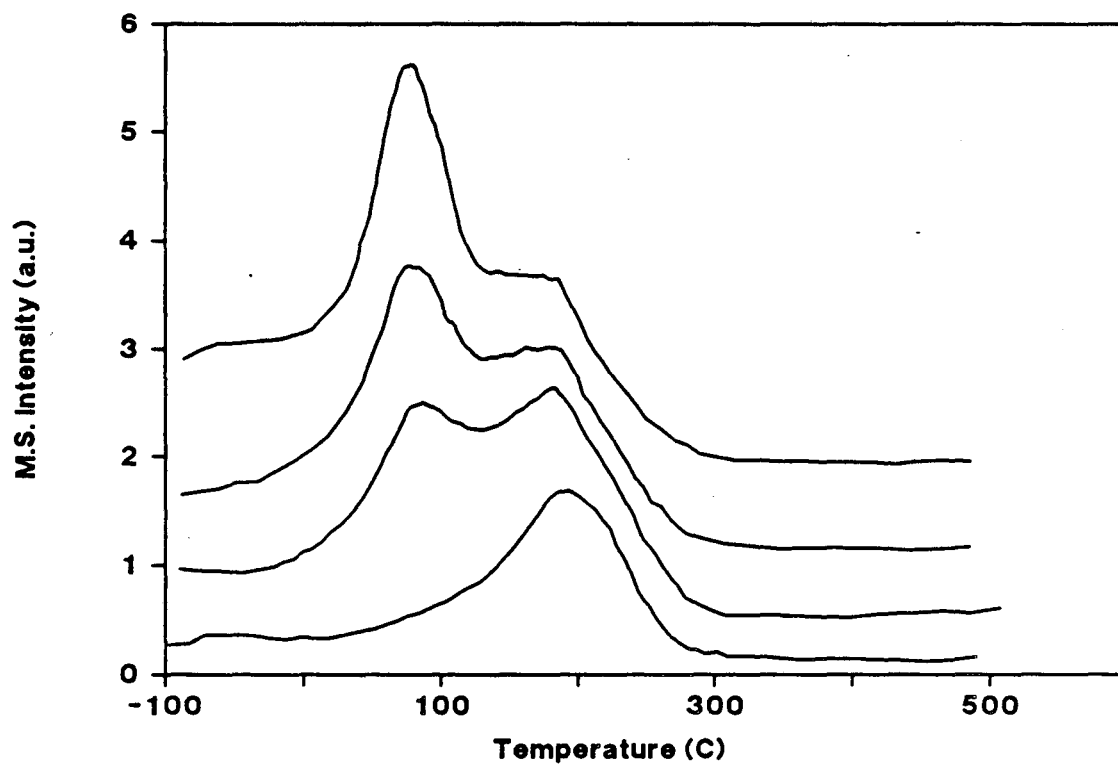


Figure 4.4. Benzene TPD traces from $\text{CoSi}_2(111)$, showing the same features as benzene desorption from $\text{Si}(111)$, though the peaks occur at slightly lower temperatures. Less desorption for a given benzene exposure occurs.

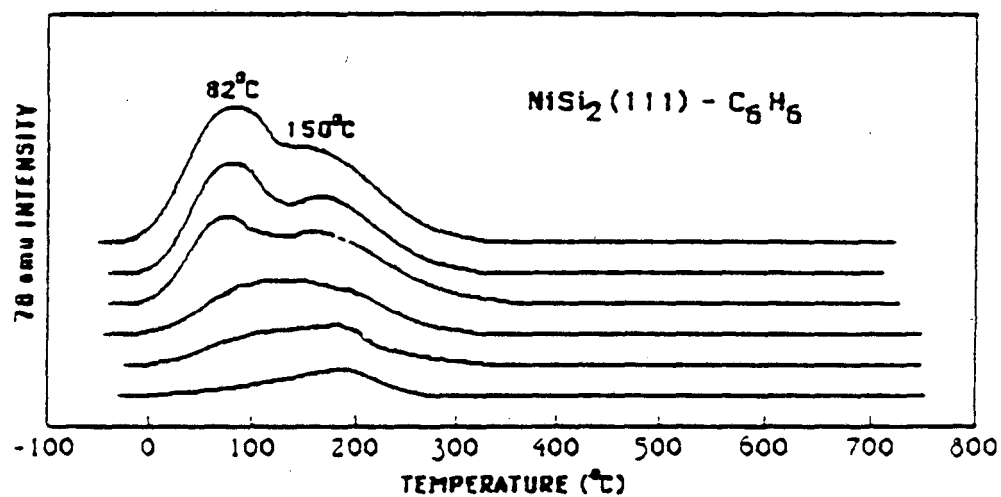


Figure 4.5. Benzene TPD traces from $NiSi_2(111)$ from Klarup,⁷ again quite similar to desorption traces from $Si(111)$ and $CoSi_2(111)$.

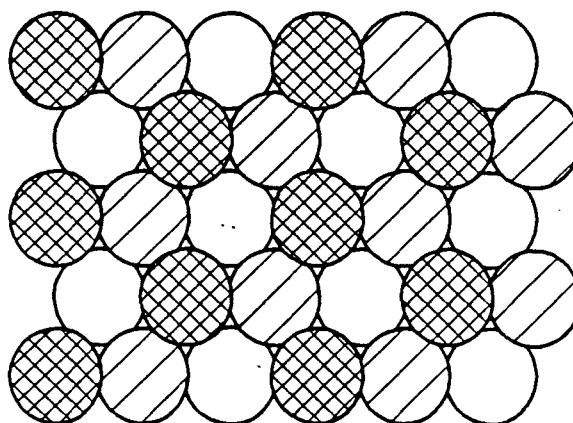
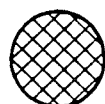
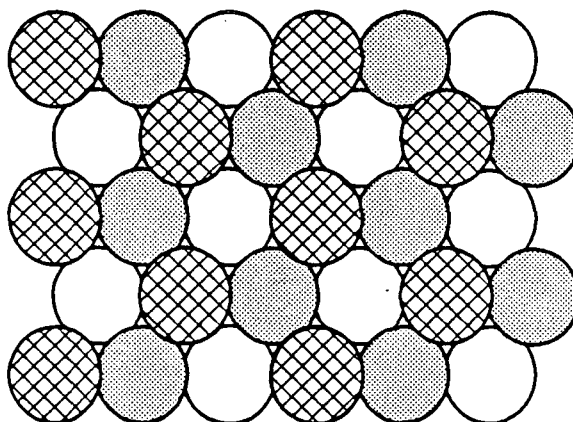
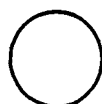
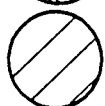
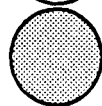
Si(111)**CoSi(111), Si-terminated****Top layer Si****Fourth layer Si****Second layer Si****Second layer Co**

Figure 4.6. Ideal (unreconstructed) surface structures for Si(111) and $\text{CoSi}_2(111)$ terminating with a single Si atomic layer, viewed from above. $\text{CoSi}_2(111)$ could also be terminated in a Si bilayer without changing the surface geometry. Third layer atoms are not visible because they lie directly under second layer atoms in the $\langle 111 \rangle$ direction. Atomic sizes for Co and Si are not to scale.

5. ALKYLIODIDE DECOMPOSITION ON Si(111)

5.1. INTRODUCTION

The use of organometallic reagents to produce thin films (organometallic chemical vapor deposition, or OMCVD) and compound semiconductor thin films (organometallic vapor phase epitaxy, or OMVPE) involves the decomposition of volatile organometallic precursors on a hot substrate, with deposition of the target species and desorption of the remaining organic fragments. Vapor deposition processes provide new synthetic materials that cannot be formed by techniques such as physical vapor deposition or sputter deposition, including many ternary and quaternary phases. OMVPE also offers the commercial advantage of producing epitaxial films without the cost and complexity of the ultra-high vacuum environment necessary for molecular beam epitaxy (MBE).

Many alkyl-substituted compounds exhibit the desired characteristics of low decomposition temperature and high volatility necessary for OMCVD and OMVPE. Alkyl group III sources are in widespread use, and efforts are underway to supplant group V hydrides with alkyl compounds.^{1,2,3} Alkylphosphines and -arsines are less toxic and less flammable than the gaseous hydrides and many are liquids at room temperature, all of which makes them much easier to handle and purify than high pressure cylinders of phosphine and arsine. In addition, alkylphosphines and -arsines decompose

at lower temperatures than the hydrides, reducing the V/III reactant ratio and giving better control of the composition of the growing compound semiconductor film.²

The wide range of alkyl ligands available enables a careful tailoring of the properties of organometallic precursors. While extensive research has gone into finding alkyl precursors to further lower the decomposition temperature, the desorption mechanisms of the surface alkyl fragments have been largely ignored. This desorption is critical to the success of any vapor deposition process, since any remaining surface carbon will be incorporated into the deposited film. In the initial stage of heteroepitaxial growth, the removal of alkyl chains from the substrate is imperative to avoid depositing carbon at the interface, possibly degrading both the epitaxial quality of the overlayer film and also the electronic properties of the resulting junction. The surface fragments remaining from incomplete desorption change the nature of the surface and so may effect the decomposition of subsequent precursor molecules.

This chapter explores the surface chemistry of adsorbed ethyl, n-propyl, and isobutyl (2-methylpropyl) groups on silicon, including the effects of surface carbon. Information on how the structures and properties of these adsorbed alkyl groups affect the thermal decomposition mechanisms and products was obtained by heating the silicon and observing the desorption products. By understanding the mechanisms of decomposition, alkyl ligands can be found that minimize the amount of incomplete desorption of surface alkyl groups.

Alkyl iodides were used to adsorb alkyl chains on Si(111) following the examples of alkyl iodide adsorption on metal surfaces.⁴ The weak C - I bond (~53 kcal/mol) makes iodides well-suited for this task. The extensively studied (111) face of Si was chosen because the surface dangling bonds are perpendicular to the surface (in the unreconstructed surface), which should simplify the possible adsorption geometries. Silicon surfaces are of practical importance for vapor deposition processes in the areas of compound semiconductor heteroepitaxy, metal deposition for contacts and interconnects, and in silicon deposition.

5.2. RESULTS

5.2.1. EtI

The first alkyl iodide studied was iodoethane (ethyl iodide, or EtI). The adsorption of EtI on Si(111) at -50°C and subsequent heating at 30°C/s produced the temperature programmed desorption (TPD) traces appearing in Figure 5.1. These traces follow the desorption of molecules having mass fragments 2, 28, 127, and 128 m/e as a function of crystal temperature. Auger electron spectroscopy (AES) demonstrates that carbon is deposited in these experiments, suggesting that the desorption of EtI is incomplete.

The desorption rate of the molecule associated with mass fragment 28 undergoes a maximum at 465°C. Additional TPD experiments of EtI on

Si(111) reveal that mass fragments 26 and 27 also have a desorption peak maximum at 465°C. The ratios of the desorption peak heights for fragments 26, 27, and 28 are the same ratios found in the published mass spectra⁵ of ethene. The identification of this desorption product as ethene is confirmed by the absence of any desorption fragments at 465°C not present in the mass spectrum of ethene.

H₂ (2 m/e⁻) has a desorption peak maximum at 580°C. Mass fragment 128 m/e⁻, which has a desorption peak occurring at 560°C, is due to the desorption of HI. Comparison of the 127 m/e⁻ trace to the 128 m/e⁻ trace indicates that additional iodine desorbs at 575°C as I₂, though this assignment of I₂ could not be verified because of the low sensitivity of the mass spectrometer above 200 m/e⁻.

Desorption of EtI is seen at the start of the heating ramp, which is due to multilayer desorption from Si(111) or desorption from the Ta supports. No intact EtI desorption is observed after this initial peak, nor does alkane desorption occur. In addition, the presence of adsorbed H on the Si(111) surface from overnight exposure to atomic H (produced by filaments such as the ion gauge) does not lead to any alkane desorption.

5.2.2. n-PrI

The adsorption of 1-iodopropane (n-PrI) on Si(111) followed by heating resulted in the TPD curves shown in Figure 5.2 for mass fragment 26 m/e⁻.

Two desorption peaks are seen for 26 m/e⁻ at 435°C and 580°C. The detection of other mass fragments for both desorption peaks appearing in the trace for 26 m/e⁻ and comparison to published mass spectra⁵ clearly identifies the first peak as propene and the second as ethene. The relative amount of propene and ethene desorption is not constant, however, and subsequent desorption experiments result in a decrease in the amount of propene desorption and a relative increase in ethene desorption (Figure 5.2). In addition, AES indicates that these successive thermal decompositions of n-PrI deposit carbon on the Si surface. Comparison to published Auger spectra reveals this carbon to be carbidic in nature, and not graphitic or diamond-like.⁶

The desorption of H₂ (2 m/e⁻), I₂ (127 m/e⁻), and HI (128 m/e⁻) again occurs at 580, 575, and 560°C respectively. No intact n-PrI desorption or other desorption products are found. In addition, exposure of the Si(111) surface to atomic hydrogen prior to TPD experiments does not lead to any alkane desorption.

The relationship between the distribution of alkene decomposition products found in Figure 5.2 and the presence of surface carbon deposited from previous desorption experiments is displayed in Figure 5.3. This Figure shows the relative amounts of propene and ethene desorption as a function of previously adsorbed carbon. Figure 5.3, like Figure 5.2, shows that increasing surface carbon leads to a decrease in the amount of propene desorption as well as a decrease in the total amount of alkene desorption. Ethene desorption increases with the initial increase in adsorbed carbon,

though it too decreases as the carbon coverage increases further.

The decrease in the molecular propene/ethene desorption ratio as a function of carbon coverage is shown in Figure 5.4. The molecular desorption ratio is a better indication of product distribution because it is not influenced by changes in the amount of n-PrI adsorption, caused by differences in the exposure of n-PrI to the surface and in the availability of adsorption sites. The relative molecular desorption rates appearing in Figures 5.3 and 5.4 were calculated by dividing the observed mass spectral signal by the normalized intensity of the 26 m/e⁻ fragment in the published mass spectra of propene and ethene. Mass fragment 26 m/e⁻ was chosen to maximize smaller ethene contribution in the total desorption trace, since 26 m/e⁻ is a less smaller peak in the mass spectrum of propene than in ethene.

Figure 5.5 shows the contributions of propene and ethene from the thermal decomposition of n-PrI on a carbon-containing Si(111) surface. The desorption peak shape for propene was found by monitoring the mass fragment 41 m/e⁻, which is the 100% peak in the mass spectrum of propene but does not appear in the mass spectrum of ethene. The trace for mass fragment 41 m/e⁻ was then scaled down and subtracted from the 26 m/e⁻ trace to yield the desorption peak of ethene. The full width at half maximum (FWHM) of the propene peak is 310°C around a desorption peak maximum at 435°C. The higher temperature ethene peak has a desorption peak maximum at 580°C and yet a far narrower FWHM of 120°C.

5.2.3. i-Bul

The top curve in Figure 5.6 shows the two peaks obtained in the TPD trace for a mass fragment of 40 m/e⁻ from the thermal decomposition of 1-iodo-2-methylpropane (isobutyl iodide, or i-Bul) on clean Si(111). The desorption products are again alkenes, in this case isobutene and propene. Isobutene desorbs at 350°C, followed by propene desorption at 470°C. The lower desorption traces in Figure 5.6 indicate that repeated thermal desorption experiments favor the formation of propene over isobutene. Not shown in Figure 5.6 are the desorption traces for 2 m/e⁻, 127 m/e⁻, and 128 m/e⁻, which again occur at 580°C, 560°C, and 575°C respectively. As in the case of EtI and n-PrI adsorption, no other desorbing species, including alkyl iodides and alkanes, are produced.

Carbon is also deposited in these experiments, and its effect favoring the desorption of propene over isobutene is found in Figures 5.7 and 5.8. As in the case of n-PrI decomposition on Si(111) (Figures 5.3 and 5.4), an increase in carbon coverage results in an increase in the amount of desorption of the smaller alkene relative to the larger one. In this case, the increasing surface carbon content favors the desorption of propene over isobutene, though the total amount of alkene desorption decreases.

5.3. DISCUSSION

The desorption products obtained in the thermal decompositions of EtI, n-PrI, and i-BuI on Si(111) indicate that several reactions occur. The most important of these for organometallic vapor deposition processes is the desorption of the intact alkyl chain. The desorption of hydrogen, which occurs at higher temperatures, is less of a concern to vapor deposition processes because H atoms readily combine to desorb as H₂. The complete alkyl desorption from EtI gives ethene desorption; propene and isobutene are the complete desorption products from n-PrI and i-BuI respectively. The desorption of shorter alkenes (ethene desorption from n-PrI, propene desorption from i-BuI) results in carbon deposition which is undesirable in organometallic vapor deposition processes. EtI, of course, cannot produce desorption of a shorter (C₁) alkene, and no methane desorption occurs. Alkene desorption is the result of dehydrogenation, both in the desorption of the entire alkyl chain and in the desorption of alkenes having one fewer carbon atom than the initial alkyl chain.

In the thermal decomposition of EtI on Si(111), both C - I and C - H bonds are broken, resulting in alkene desorption. The first step in this dehydrogenation mechanism is most likely the scission of the weak C - I bond, yielding an adsorbed ethyl group, though these experiments cannot distinguish between dissociative adsorption of the EtI and C - I bond breakage occurring upon heating. Low temperature C - I bond breaking has been observed for alkyl iodides adsorbed on metals, where high resolution electron energy loss spectroscopy found the C - I bond of methyl iodide

adsorbed on Pt(111) to break between -23 and -13°C.⁴ Further evidence that C - I bonds break before C - H bonds is found in the thermal decomposition of n-PrI on Si(111). Here, the temperature at which HI desorbs is lower than the desorption temperature of ethene, showing clearly that C - I bond breakage has occurred before ethene desorption.

The decomposition that results in ethene desorption from adsorbed n-EtI is a dehydrogenation reaction involving abstraction of the β H. This mechanism applies to intact alkene desorption from EtI, n-PrI, and i-Bul because the alkyl chains only differ in the number of carbon atoms bonded to the β C. Figure 5.9 shows the desorption mechanism of propene from n-PrI occurring in a single step, though a two step mechanism proceeding via a radical intermediate cannot be ruled out. A radical mechanism would be expected to require a significantly higher activation energy, however, and any mechanism involving charge separation would require far more energy still. A similar one step mechanism also explains the dehydrogenation which leads to ethene desorption from adsorbed n-PrI (Figure 5.9). In this case, a γ H instead of a β H is abstracted from the adsorbed n-propyl group by the Si surface. The bond between the α C and β C is broken and ethene desorbs, leaving behind adsorbed CH₂. A radical mechanism is possible here as well, though the activation energy would be even higher than in the case of β H abstraction, since the radical formed is now primary instead of secondary.

The geometry of an adsorbed n-propyl chain (and an ethyl chain) is favorable for both β and γ H abstraction. Figure 5.10 shows such a

geometry for β H abstraction, with the β H at its closest approach to the Si surface, only 1.60 Å away. This distance is quite reasonable for H abstraction by the surface, since it is just slightly longer than the typical Si - H bond length of 1.48 Å. These geometries were calculated using values of 1.54 Å and 1.10 Å for the C - C and C - H bond lengths respectively and assume alkyl adsorption on a Si atop site (i.e. directly over a top layer Si atom). The actual distance between the β H and a surface atom depends of course on the configuration of the n-propyl chain, the adsorption site of the β C (atop, bridging, 3-fold site, etc.), and the type of surface site under the β H. β abstraction can also be pictured as proceeding through the 5-membered (or 6-membered, when 3 Si atoms are included) cyclic transition state common in organic chemistry. For γ abstraction, the distance between the surface and the γ H for the configuration shown in Figure 5.10 is 1.62 Å, indicating that γ abstraction is also geometrically feasible.

The dangling bonds of the surface of Si(111) result from the directional bonding of covalent semiconductors. The tetrahedral coordination of Si is not satisfied in the top layer, leading to orbitals that extend from the surface at 90°. This orbital is available for bonding and contains one electron. Both the adsorption of an alkyl chain directly on an atop site and the abstraction of a hydrogen atom by a dangling bond are likely because bonding to C or H will satisfy the tetrahedral bonding requirements of a top layer silicon atom.

While the desorption temperature and energy is less for propene than ethene, ethene desorption still occurs. In addition, repeated thermal

desorption experiments indicates that the presence of surface carbon favors ethene desorption over propene (Figures 5.2, 5.3, and 5.4) and thus promotes further carbon deposition. This trend favoring the higher desorption energy (E_a) pathway with increasing carbon coverage is attributed to the blocking of β H abstraction sites by carbon. Without this adsorbed carbon, (or at least with minimal adsorbed carbon), the overwhelming desorption product is the intact alkene. This alkene has the lower activation energy of desorption because it results from β instead of γ abstraction. β H abstraction from an adsorbed n-propyl group requires less energy than γ H abstraction because the β C is secondary while the γ C is primary. With increasing surface carbon, the higher temperature γ abstraction route becomes more important.

The blocking of β H abstraction sites by carbon is a result of a smaller number of abstraction sites available to the β H compared to the γ H. Figure 5.10 shows the radii of travel of the β and γ H within a reasonable abstraction distance from the surface for an adsorbed n-propyl or isobutyl group. The nearest radii for both β and γ H were found in configurations having the smallest surface - H separation. For the furthest radius of the β H, a maximum H abstraction distance of 2.45 Å was assumed, making the β C and β H equidistant from the Si surface. The configuration displayed in Figure 5.10 shows the γ H at its furthest distance from the adsorption site. When superimposed on an ideal, unreconstructed Si(111) surface (Figure 5.11), these radii define the likely H abstraction sites. The preferential desorption of ethene results from the blocking of the β H abstraction sites.

From Figure 5.11 it follows that for a random distribution of adsorbed carbon, far more abstraction sites are available to the γ H, favoring ethene desorption.

For the thermal decomposition of i-Bul on Si(111), abstraction of the β H and γ H result in isobutene and propene desorption respectively. The β and γ dehydrogenation mechanisms and geometries presented for n-PrI decomposition also apply to the decomposition of i-Bul, since the carbon skeletons of the adsorbed n-propyl and isobutyl groups are almost identical. The only difference is the substitution of the β carbon, which makes the β H tertiary instead of secondary as in an n-propyl chain. This should lower the energy necessary to abstract the β H, thereby lowering the desorption temperature and energy of the intact alkene. Figure 5.6 shows this to be the case, as the desorption temperature of isobutene from i-Bul is 85°C lower than the desorption temperature of propene from n-PrI.

In spite of this increased ease of abstraction of the β H relative to the γ H, the desorption of propene demonstrates that γ H is still abstracted. Figure 5.8 shows that the presence of additional surface carbon favors further propene desorption, which is the same trend in dehydrogenation mechanism observed for n-PrI decomposition (Figure 5.4). The blocking mechanism of carbon responsible for ethene desorption from n-PrI is also at work here. The rate at which the alkene ratio decreases is much faster in the case of i-Bul decomposition, however, and the final alkene ratio is lower as well. This is inconsistent with the lower energy necessary to abstract a tertiary rather

than a secondary β H, and thus is probably a consequence of the reduction in the number of β H from two in n-PrI to one in i-Bul.

Propene desorption from i-Bul and n-PrI does not occur at the same temperature, which is not unexpected since propene desorption from n-PrI involves abstraction of a secondary H and Si - C breakage, but from i-Bul propene requires primary H abstraction and C - C bond breakage. The γ dehydrogenation products from i-Bul and n-PrI also have different desorption temperatures, and while they both involve primary H abstraction, the differing substitution of the β C changes the energy needed to break the α C - β C bond that results in alkene desorption.

A difference in dehydrogenation mechanisms is suggested by the shapes of the desorption curves of first and second peaks, both for n-PrI and i-Bul. In the case of n-PrI adsorbed on Si(111), the propene and ethene peaks have FWHM's of 310°C and 120°C respectively. These peaks are far wider than would be predicted using the simple Redhead rate equation⁷

$$R_{\text{des}}(t) = -dN/dt = \nu N e^{-E_a/kT} \quad (1)$$

for first order desorption and a linear heating rate. Calculating peak widths using the above equation gives FWHM's of 56°C and 67°C for the first and second desorption peaks respectively. Not only are the observed peaks much wider, the expected trend of increased peak widths at higher desorption temperatures is reversed. This calculation uses the typical value of 10^{13} s^{-1}

for the pre-exponential factor (ν) and a heating rate of 30°C/s, the same as that used experimentally. The activation energies of desorption obtained using these values are 42 kcal/mol and 51 kcal/mol for the first and second peaks respectively. To increase the calculated FWHM of the first desorption peak to the 310°C width observed experimentally requires a ν of 8.8 s⁻¹. Using this value for ν yields an E_a of only 5.6 kcal/mol. Matching the experimental FWHM of 120°C for the second peak changes the ν to 3.8×10^6 s⁻¹ and gives $E_a = 26.7$ kcal/mol. Both of these frequency factors are far lower than the 10^{16} to 10^{17} s⁻¹ range expected for immobile adsorbates. The low frequency factors and the calculated E_a of 5.6 kcal/mol for propene desorption, while able to mathematically model the n-PrI TPD results, are not realistic values.

Alternatively, a combination of several narrow desorption peaks with slightly different peak temperatures might also produce the observed wide peak shape. If the rate-determining step in desorption is the Si - C bond breaking, then a range of E_a 's and consequently a wide desorption peak could be caused by the difference in Si - C bond energies resulting from a variety of alkyl chain adsorption sites on the Si(111) surface (atop, bridging, or 3-fold hollow). In this scheme, the second peak must be narrower because the rate-determining step is the C - C bond breaking which has a single activation energy for bond breaking, unlike the range of E_a for Si - C bonds caused by differences in adsorption sites.

The other candidate for the rate-determining step is the abstraction of H from the alkyl chain. The various possible H abstraction sites on the Si(111) surface produce a range of E_a 's and consequently a wider observed desorption peak. The major drawback of this scheme is that it cannot account for the difference in width between the first and second peaks, especially since the γ H has a much larger radius of travel and so would be exposed to a larger variety of H abstraction sites than the β H. The difference in the desorption temperatures of the β dehydrogenation products from n-PrI and i-Bul suggests, however, that H abstraction is indeed involved in the rate-determining step, making desorption a one step process in which the rate-determining step involves both C - H and either C - Si or C - C bond breaking.

5.4. CONCLUSIONS

The thermal decomposition of n-PrI and i-Bul on Si(111) results in the desorption of alkenes, HI and I_2 . For each iodide, β and γ dehydrogenation occurs, with n-PrI producing propene and ethene and i-Bul giving isobutene and propene. Surface carbon blocks the abstraction of β H and results in an increase in γ dehydrogenation for both alkyl chains. The difference in peak widths for the first and second peaks suggests different desorption mechanisms for β and γ dehydrogenation.

The incomplete desorption of adsorbed alkyl chains and consequential deposition of carbon found in this work present serious difficulties in the use of alkyl precursors for deposition processes on Si(111) surfaces. While alkyl chain decomposition on clean, carbon-free silicon surfaces results in comparatively little carbon deposition, such carbon increasingly favors incomplete alkyl chain desorption and further carbon deposition. This makes it imperative that any carbon present on the surface be removed before any alkyl vapor deposition process takes place.

To lower the amount of carbon deposition from organic precursors it may be necessary to look past the simple alkyl compounds. The successful desorption mechanisms are those that do not deposit carbon. These mechanisms all involved β dehydrogenation, so the key may be lowering the β H abstraction energy (i.e. increasing the stability of the resulting radical). This could be achieved by delocalizing the radical through a conjugated system, such as in a vinyl or phenyl group. Electron releasing groups such as hydroxide also stabilize radicals and so are also candidates. The optimal route may be a combination of delocalizing and electron-releasing groups on the β C ("capto-dative" or "mero" stabilization), which is known to produce exceptionally stable radicals.⁸ Since the desorption mechanism involved here is most likely a one-step process, the breaking of the surface - α C bond must not be overlooked.

It would be of great technological importance to explore the desorption of alkyl groups from compound semiconductor surfaces. The literature reports

a variety of desorption mechanisms from alkyl precursors including the combination of two alkyl groups which result in alkane desorption, the combination of adsorbed H with an alkyl group and alkane desorption, and the dehydrogenation mechanism observed in this work.⁹ The UHV techniques used here would be well suited to the preparation and characterization of these compound semiconductor surfaces and the exploration of the alkyl desorption mechanisms using alkyl iodides.

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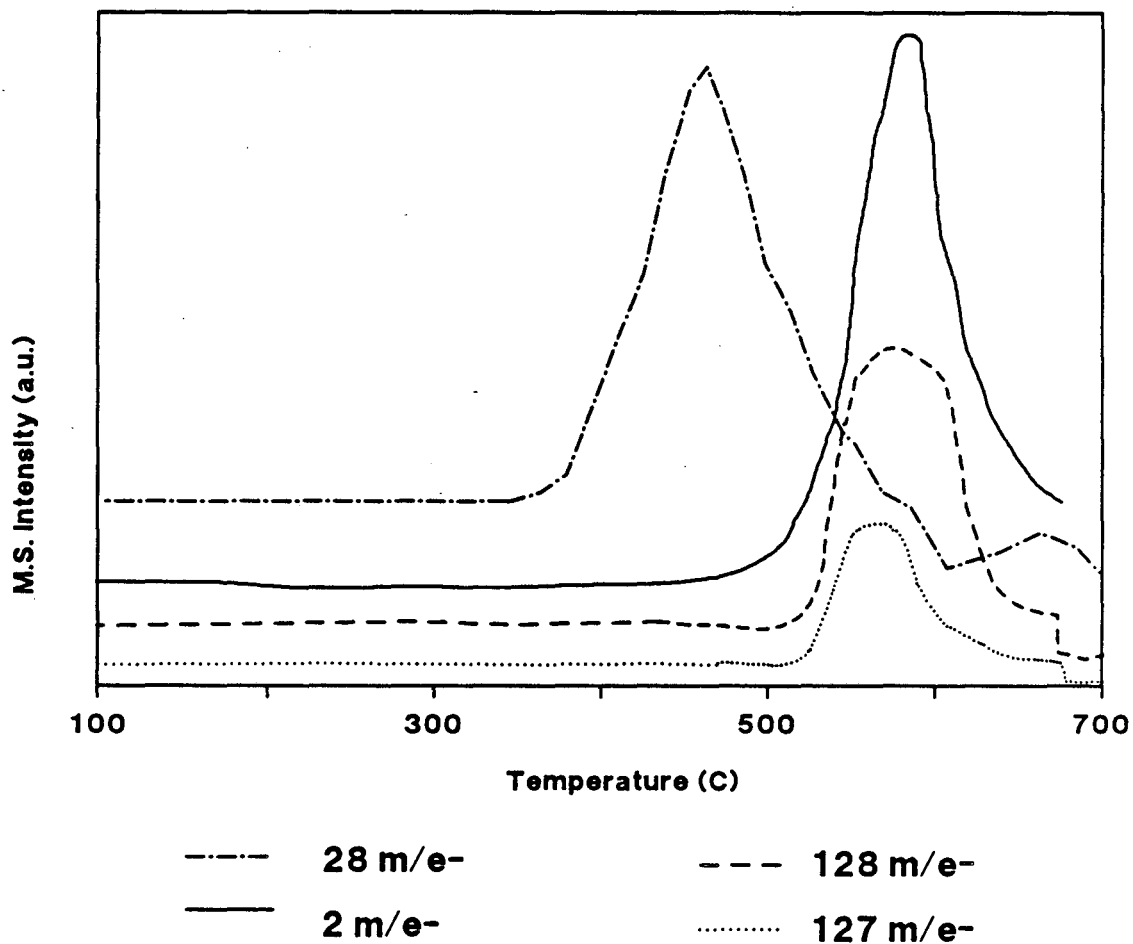
Etl TPD on Si(111)**28 m/e-**

Figure 5.1. TPD traces for mass fragments 2, 28, 127, and 128 m/e⁻ for EtI adsorbed on Si(111). Fragment 28 m/e⁻ monitors the desorption of ethene; iodine (127 m/e⁻) desorbs as HI and I₂.

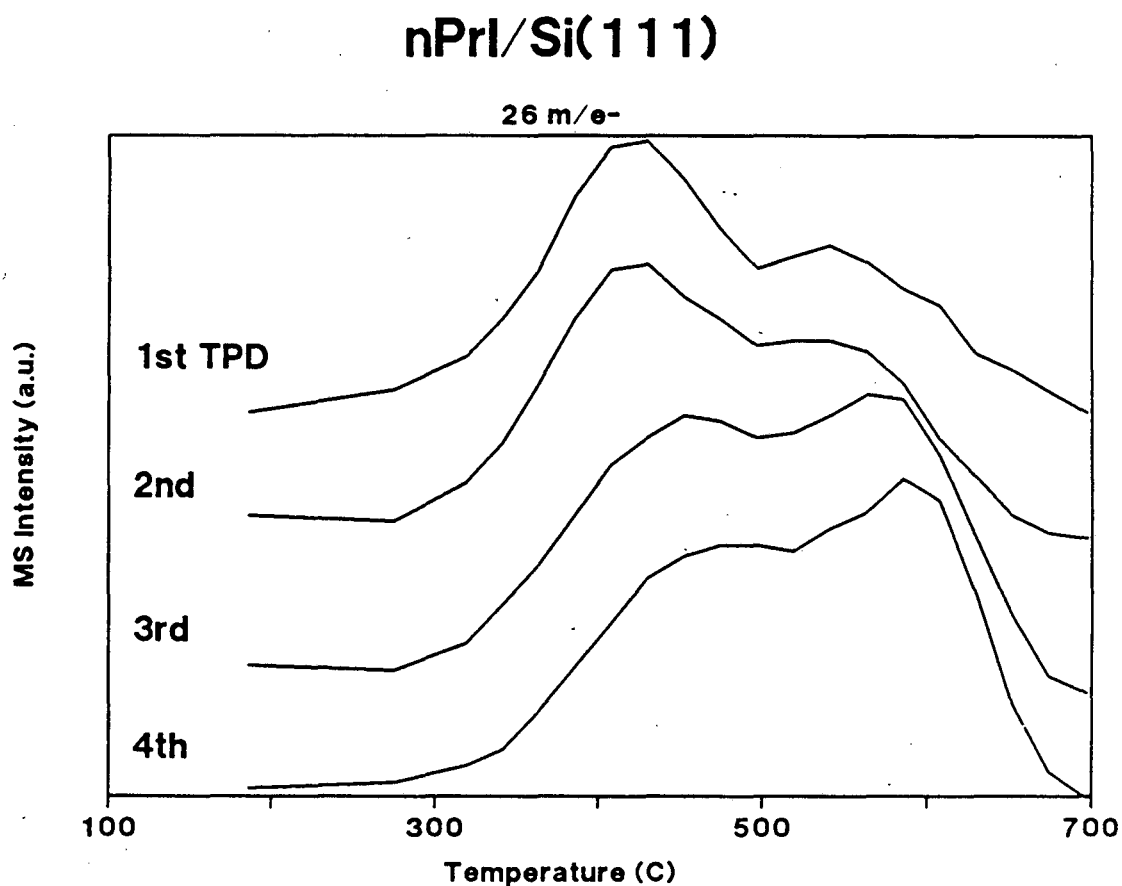


Figure 5.2. Traces for successive n-PrI TPD experiments for 26 m/e⁻. The lower and higher temperature peaks in the trace of 26 m/e⁻ are due to propene and ethene respectively. Subsequent experiments indicate an increase in the amount of ethene desorption (higher temperature peak) and a decrease in the amount of propene desorption (lower temperature peak).

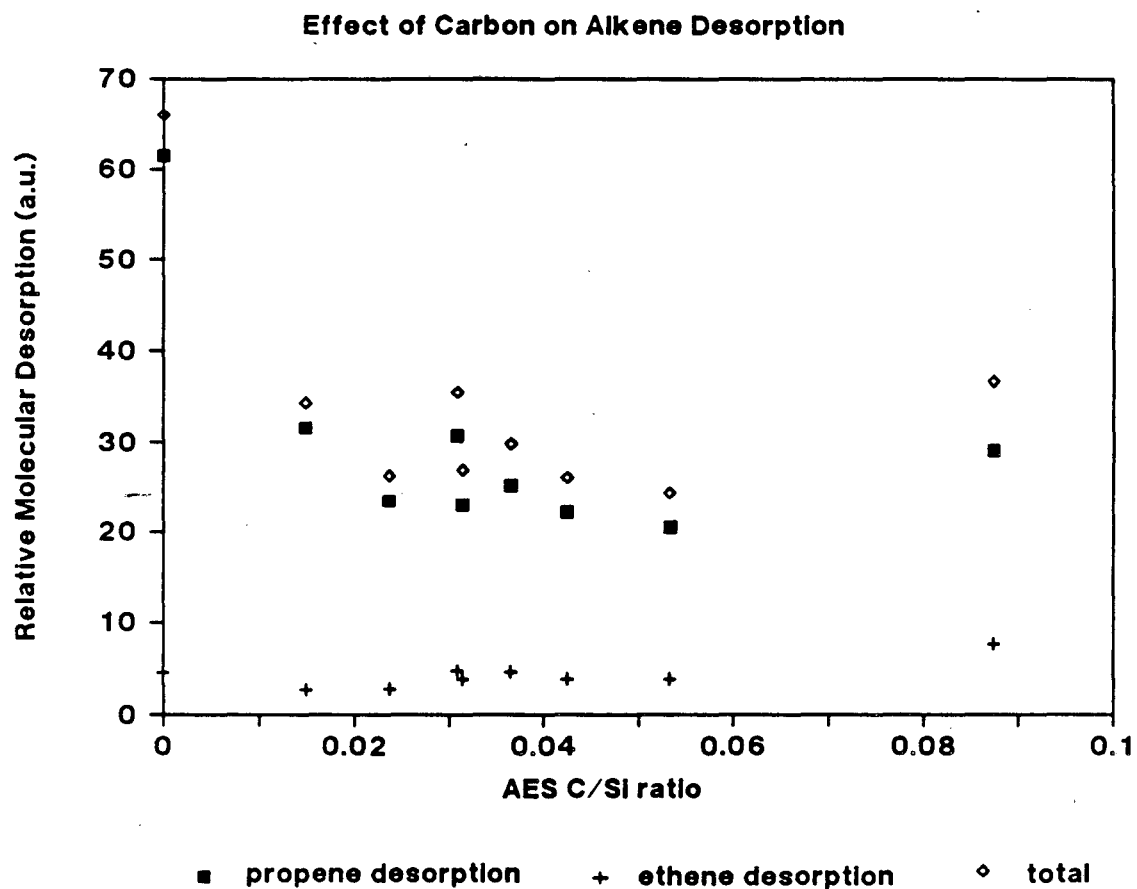
n-PrI/Si(111)

Figure 5.3. The effect of surface carbon on the thermal decomposition products of n-PrI, indicating the relative amounts of propene and ethene desorption together with the total amount of alkene desorption.

n-PrI/Si(111)

Effect of Carbon on Alkene Desorption

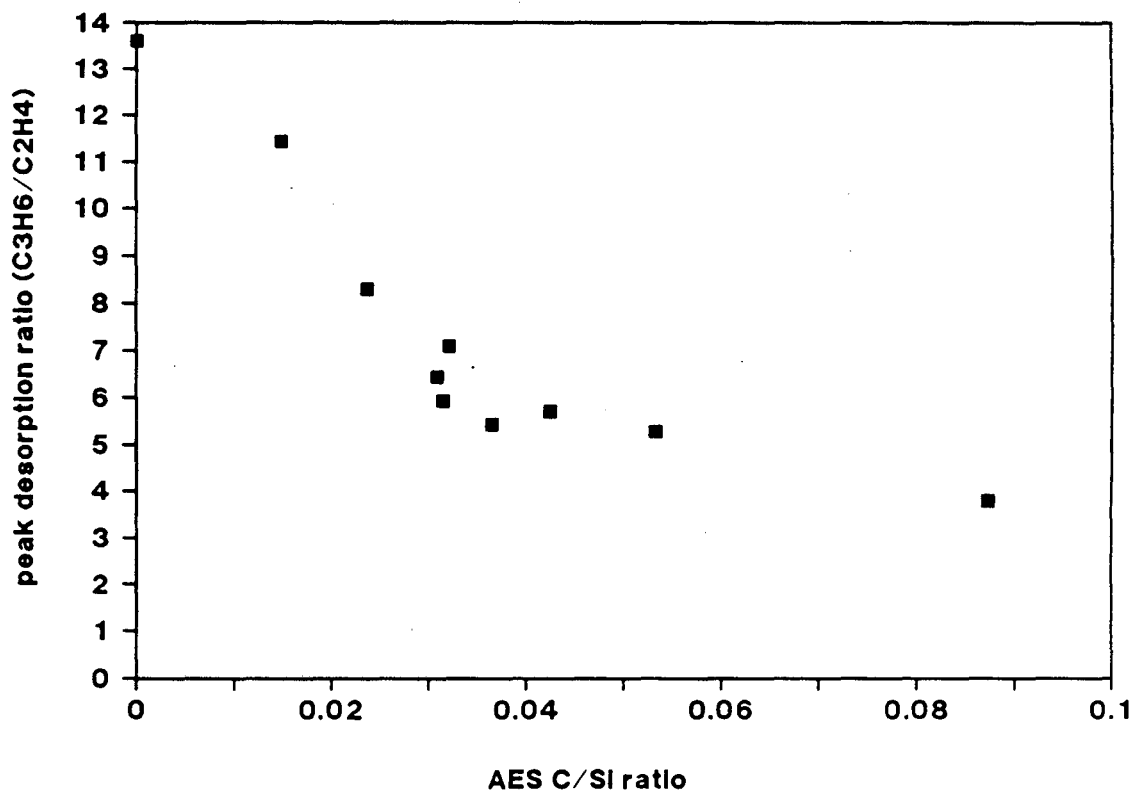


Figure 5.4. The effect of adsorbed carbon on propene/ethene desorption ratio.

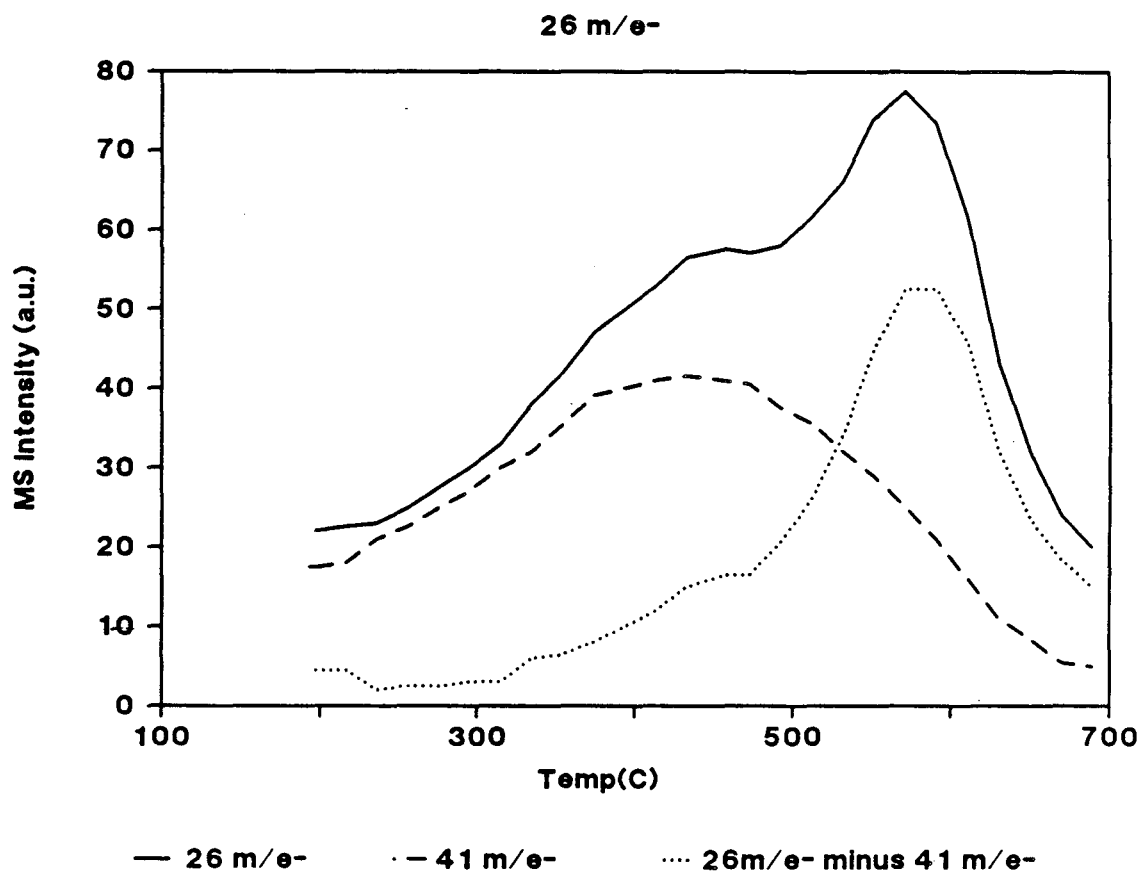
n-PrI/Si(111)

Figure 5.5. Contribution of propene, ethene in 26 m/e⁻ TPD trace for n-PrI. The contribution of ethene was obtained by subtracting a scaled TPD trace of 41 m/e⁻, which only represents propene desorption, from the trace of 26 m/e⁻.

i-Bul/Si(111)

40 m/e-

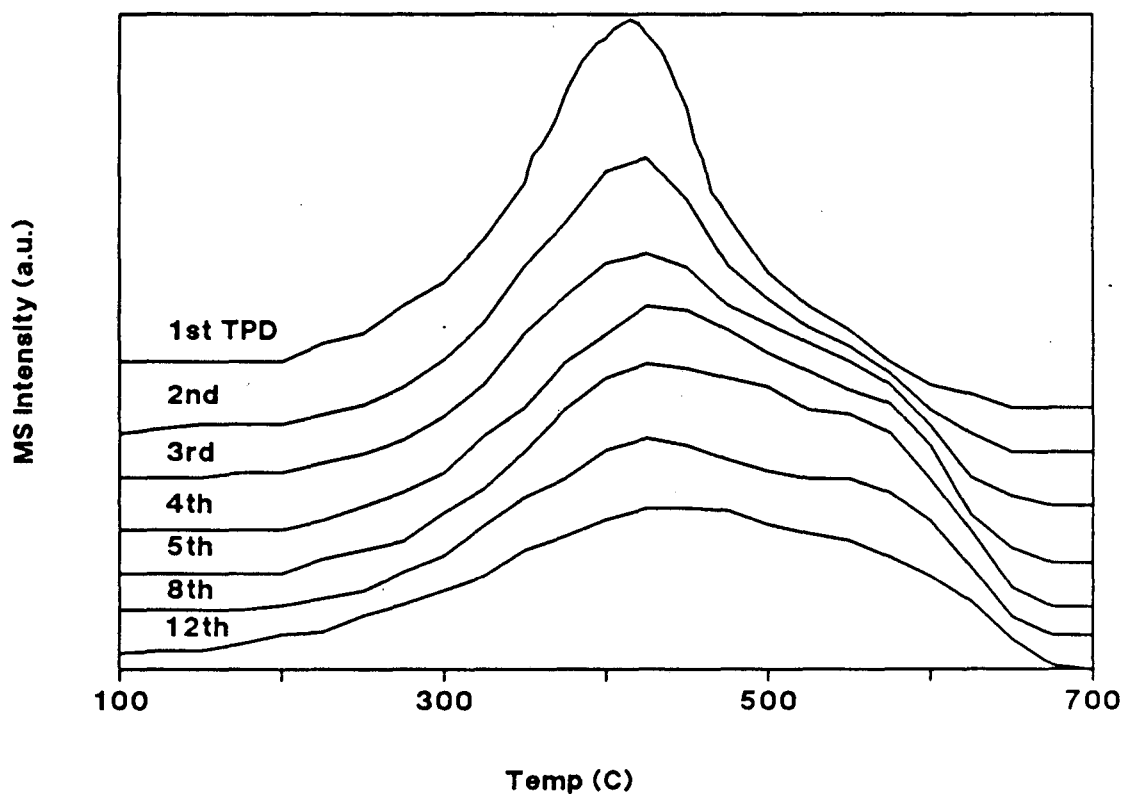


Figure 5.6. 40 m/e⁻ TPD traces for i-Bul adsorbed on Si(111). As in the thermal decomposition of n-PrI, successive TPD experiments favor the production of the higher temperature desorption product (here propene) over the lower temperature one (isobutene).

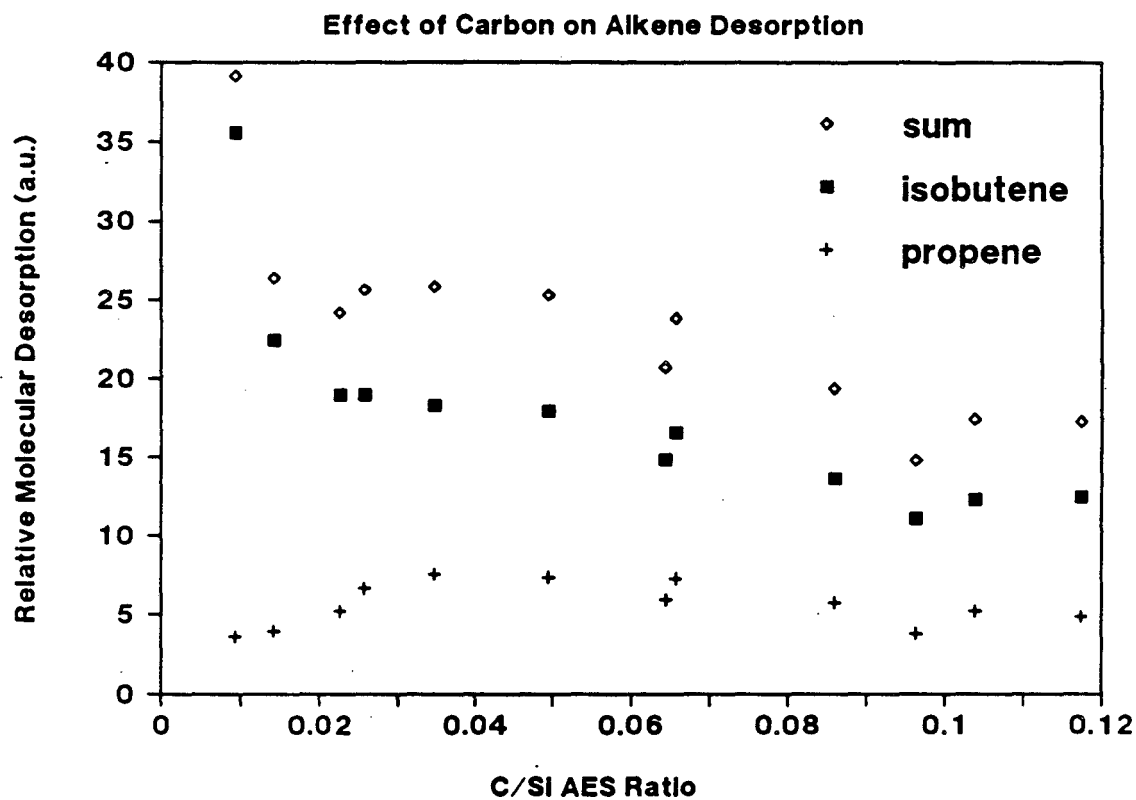
i-Bul/Si(1 1 1) TPD:

Figure 5.7. The effect of adsorbed carbon on the relative and total amounts of isobutene and propene desorption.

i-Bul/Si(111) TPD:

Effect of Carbon on Alkene Desorption

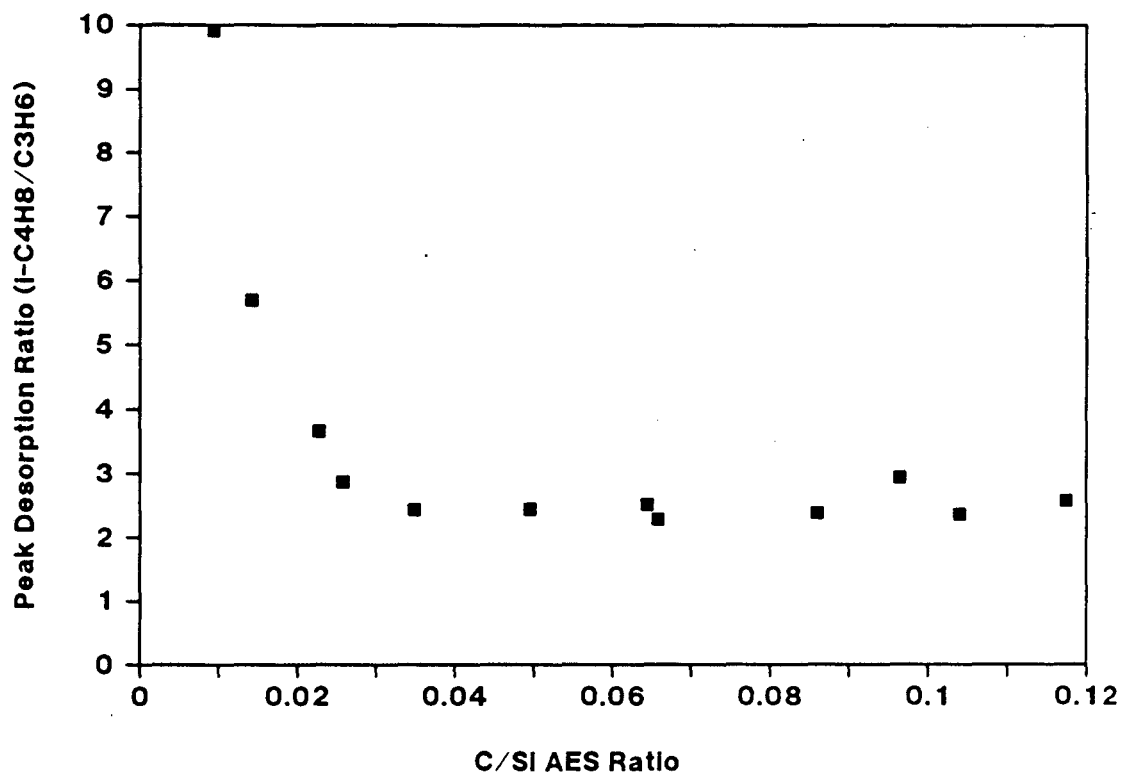


Figure 5.8. Effect of adsorbed carbon on isobutene/propene desorption ratio.

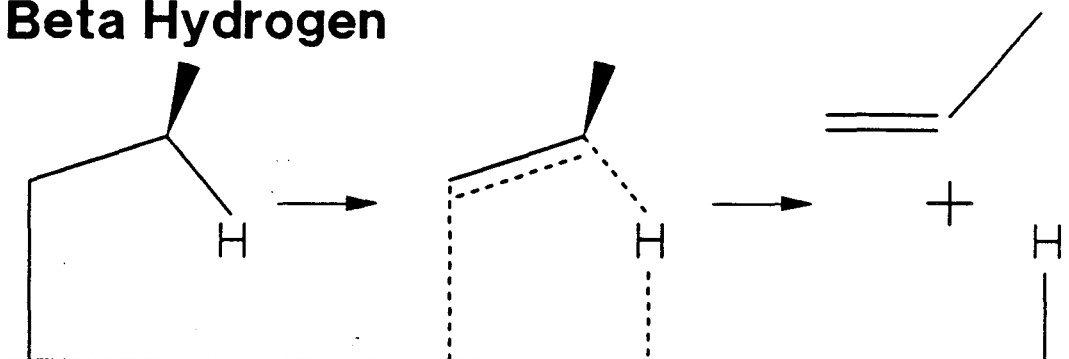
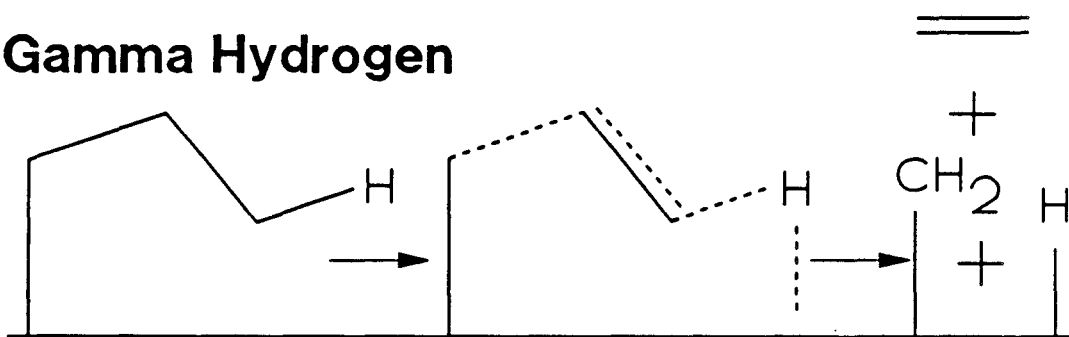
Beta Hydrogen**Gamma Hydrogen**

Figure 5.9. Diagram for β and γ H abstraction, showing hydrogen abstraction and alkene desorption occurring in a single step. A two step mechanism proceeding through a radical intermediate is also possible but would require a higher activation energy.

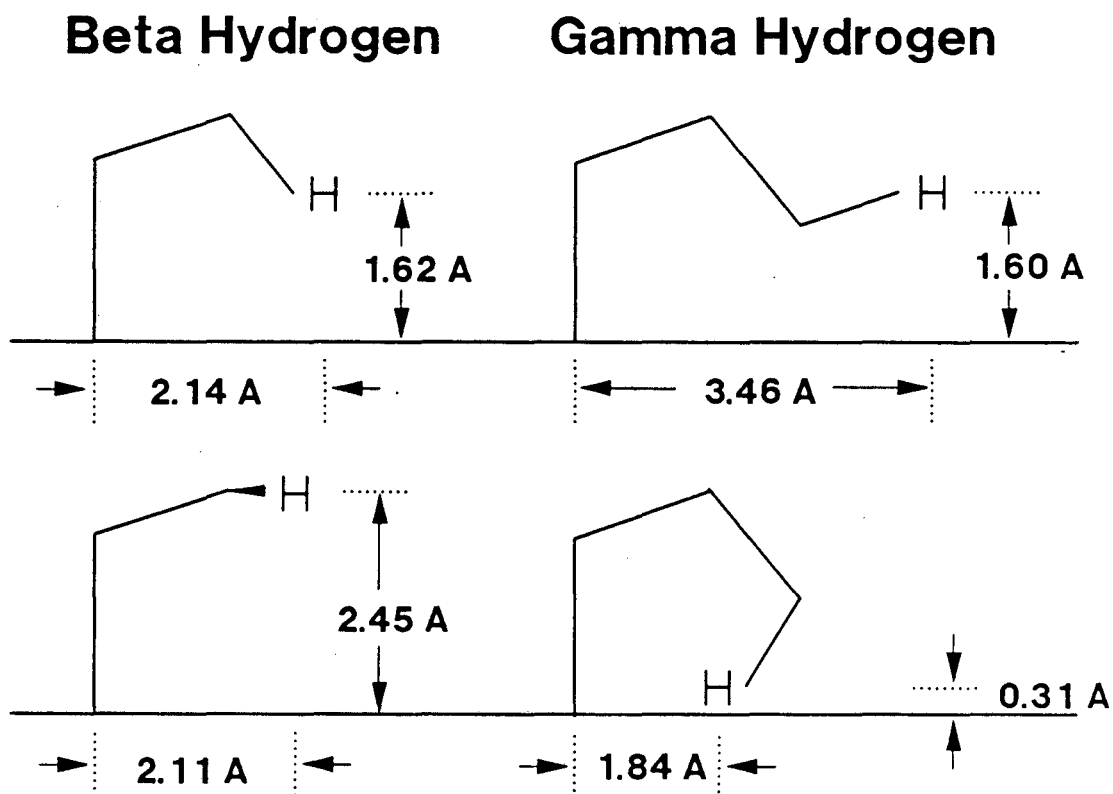


Figure 5.10. Geometry for β and γ H abstraction, displaying the configurations of the adsorbed alkyl chains for the nearest and furthest lateral approach of β and γ H from the chain adsorption site. The vertical distances shown are from the plane of the surface to the H atom. All surface - H distances are quite reasonable for H abstraction by a surface dangling bond.

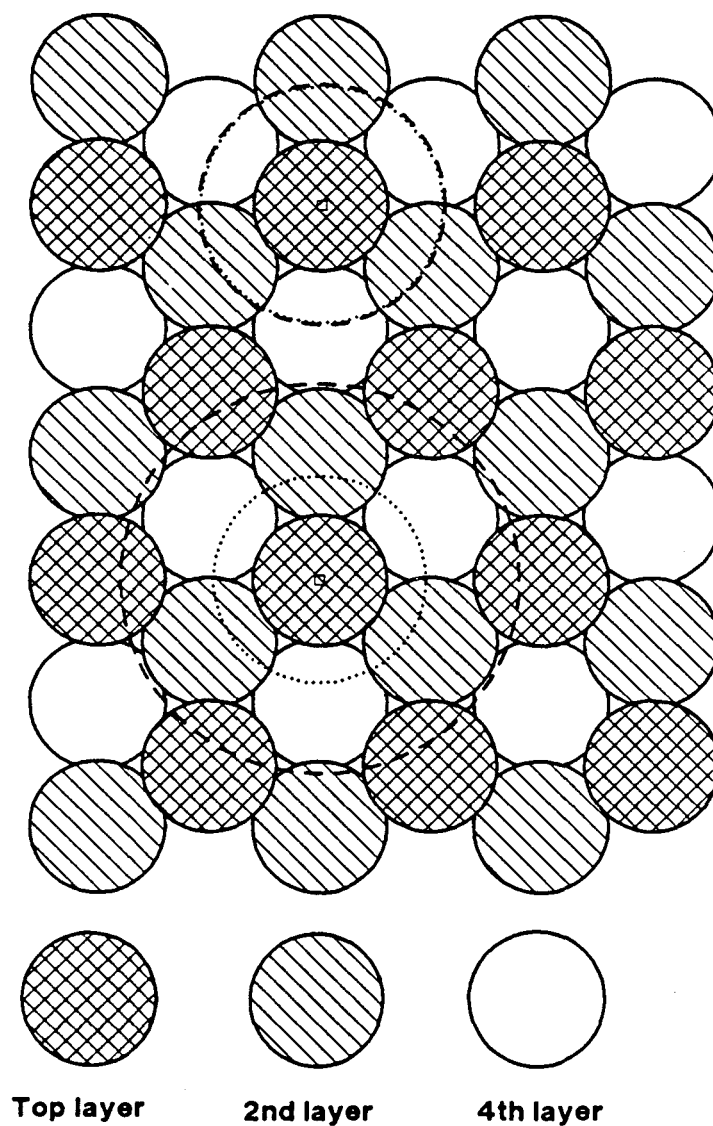


Figure 5.11. Radii of travel of H, superimposed on an ideal, unreconstructed Si(111) lattice ("bulk-like termination"). The dashed and solid circles depict the nearest and furthest approaches of β and γ H for the configurations shown in Figure 5.10. The radii represent horizontal displacements of H from a top layer Si adsorption site.

6. CONCLUSIONS

The experiments described in this thesis all investigate reactions that occur on Si(111) surfaces. The reactions of Si(111) with Co are of interest because they provide insight into the formation of the technologically important material CoSi_2 . The growth of CoSi_2 from the reaction of Co with clean Si(111) was studied and compared to CoSi_2 growth on Si(111) surfaces modified with oxygen and nitrogen. The interactions of epitaxial CoSi_2 surfaces with oxygen and benzene were also studied. The thermal decompositions of alkyl iodides on Si(111) address the desorption of molecular fragments produced by CVD processes, a critical surface reaction that has been ignored in the chemical literature.

The initial deposition of Co on Si(111) was found to alter the chemical state of surface Si atoms, indicating that reaction between Co and Si takes place at room temperature. The formation of Co silicides was studied by first depositing a thicker Co layer (35 Å) on Si(111) and heating the sample, monitoring the surface composition of the resulting silicide products with Auger electron spectroscopy (AES). The use of an ultra-high vacuum (UHV) environment in the execution of these experiments kept the initial Co/Si interface free of impurities, a precaution not taken in most literature reports of Co silicide phase formation. The evolution of the silicide phases was accompanied by changes in the lineshape of the Si (LVV) Auger peak, and was consistent with the sequential formation of Co_2Si , CoSi , CoSi_2 . The final

surface of CoSi_2 , obtained after heating to 700°C , displayed a 7×7 surface reconstruction, possibly due to the formation of CoSi_2 islands on a bare, 7×7 Si surface.

The initial Co/Si interface was also intentionally modified with oxygen and nitrogen to investigate the effect of interfacial impurities on silicide formation. Oxygen and nitrogen both form stable compounds with Si that retard the diffusion of Co into the Si substrate. These compounds delayed the formation of silicide phases until higher temperatures were reached. The retarded diffusion of Co into Si also explains the observation of simultaneous Co_2Si and CoSi formation reported in studies not undertaken under atomically clean UHV conditions. As the diffusion of Co is restricted and the temperature increases, CoSi is able to form between Co_2Si and the Si substrate before all of the initial Co layer is consumed in the formation of Co_2Si . After the Co has reacted with the Si(111) substrate, the oxide or nitride layer remains on the surface of the silicide film.

The surface chemistry of epitaxial $\text{CoSi}_2(111)$ films was investigated by reactions with oxygen and benzene. Oxidation of CoSi_2 films produced a surface Si oxide, judging by the shape of the Si (LVV) Auger peak. Heating caused this surface oxide to disappear, presumably by SiO sublimation. The evolution of the Si (LVV) Auger peak after oxidation and SiO sublimation of a 7×7 CoSi_2 surface suggests the presence of a continuous CoSi_2 film, which reverts back to a 7×7 silicide surface with continued heating. If the 7×7 surface consists of silicide islands on a Si(111) 7×7 surface, then oxidation

and SiO sublimation result in a continuous silicide film. This film quickly forms islands on Si(111) again, judging by the final AES lineshape and 7×7 surface reconstruction.

The surface chemistry of CoSi_2 was also studied using temperature programmed desorption (TPD) to examine the π bonding of benzene to the CoSi_2 surface. These experiments are the first TPD investigations performed on CoSi_2 surfaces. The TPD results of benzene adsorbed on CoSi_2 are quite similar to those of benzene on Si(111), though the activation energy of desorption (E_a) of benzene from $\text{CoSi}_2(111)$ is lower. The similarity of these TPD results suggests that the surface of $\text{CoSi}_2(111)$ terminates with at least one plane of Si(111) atoms.

The study of the thermal decomposition of alkyl iodides provides insights into the chemistry of alkyl chains adsorbed on Si(111). The desorption of alkyl chains is crucial to the success of chemical vapor deposition (CVD) processes that use alkyl-substituted precursor molecules. To date, no investigations of CVD processes have focused on the desorption of alkyl species. In these studies, all alkyl groups desorb as alkenes, accompanied by H_2 desorption. Unfortunately, the desorption of surface alkyl chains was incomplete, which resulted in the deposition of carbon on the Si surface. Alkyl chain dehydrogenation was explained by the abstraction of a β or γ H by a dangling Si surface bond, resulting in alkene desorption. Dehydrogenation and desorption most likely occur by a single-step, radical mechanism. The presence of surface carbon favors γ H abstraction over β H

abstraction and produces additional carbon deposition.

The work described in this thesis contributes to the understanding of the surface chemistry of Si(111). Of the results reported here, several issues remain unresolved. The identification of CoSi_2 island formation on Si(111) at 700°C might be possible by studying TPD of C_2H_4 , where the desorption products from the two surfaces are different. C_2H_4 desorption has been used to verify NiSi_2 island formation by Klarup.¹ In the studies of alkyl surface chemistry on Si(111), it should be possible to improve the amount of intact alkene desorption by choosing an alkyl group that lowers the energy needed to abstract a β H and also lowers the energy necessary to break the bond between the alkyl group and the Si surface.

6.1. REFERENCES

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APPENDIX A. X-RAY DIFFRACTION OF THICK CoSi_2 FILMS

A.1. INTRODUCTION

The deposition of Co on Si, followed by annealing to temperatures above 500°C , has been shown by numerous researchers to produce CoSi_2 films on Si(111).¹⁻⁸ CoSi_2 films grown in this manner were characterized by a variety of techniques including Rutherford backscattering spectroscopy (RBS), X-ray diffraction, electron energy loss spectroscopy (EELS), and transmission electron microscopy (TEM) and diffraction. In this thesis, CoSi_2 films were prepared by depositing Co films on Si(111) and heating above 500°C . These CoSi_2 films were characterized using Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The Auger spectrum of CoSi_2 is distinguished from that of Si by the presence of Co as well as by the change in the shape of the Si (LVV) Auger peak (Figure 4.1). In addition, LEED demonstrates that CoSi_2 surfaces can have 7×7 or 1×1 surface reconstructions depending on the annealing temperature.

A.2. RESULTS

To prove beyond any doubt that the Co-containing surfaces studied in this thesis were indeed CoSi_2 and not Si(111) surfaces having a surface reconstruction produced by Co, the X-ray diffraction pattern of a thick CoSi_2

film was obtained. This film was grown on a Si(111) substrate that was chemically cleaned and then etched in HF prior to loading in the evaporation chamber. The wafer was transported in air from the HF bath to the evaporation chamber and so had re-grown a native oxide on the surface prior to Co evaporation. In addition, the base pressure of the evaporator was 10^{-7} Torr, making additional surface contamination during evaporation likely. 700 Å of Co was then deposited on the Si wafer by resistively heating a tungsten boat that held the Co source, which was a pressed pellet of Co powder. The thickness of the Co deposition was monitored using a quartz microbalance.

Next, the sample was transferred to the ultra-high vacuum (UHV) chamber used in the experiments described in this thesis. The surface of the sample was sputtered with Ar ions to remove surface oxygen and carbon contamination and then annealed at 1000°C to react the Co and Si(111). Heating was continued at 1000°C until the Auger spectrum of the surface no longer changed with time. AES revealed that the final surface contained Co and Si and only small amounts of C and O. Visual inspection of the surface of the sample showed it to be rough only where Co had been deposited. Regions of bare Si existed where the Si was held during Co evaporation; these regions remained smooth and shiny. Faint first order LEED spots were observed in a hexagonal pattern, along with higher order spots near the first order spots. These higher order spots were observed between first order spots, but only the higher order spot next to the first order spot could be seen. These higher order spots may have been 7th order (i.e. indicating a 7

$\times 7$ surface reconstruction) but only a definite assignment of at least 5th order could be made.

The X-ray diffraction pattern of this film appears in Figure A.1, showing only peaks corresponding to CoSi_2 and Al. The Al peaks were due to the Al sample holder (no Al was detected in the sample by AES). In the range of $20^\circ < 2\theta < 75^\circ$ only two strong CoSi_2 peaks were found. The strongest is the (111) peak (at $2\theta = 28.3^\circ$; $d = 3.14 \text{ \AA}$ using Cu K_α radiation). The second peak occurs at $2\theta = 48.3^\circ$ and is the (220) reflection. Extremely faint peaks are seen at angles corresponding to (311) and (400) CoSi_2 reflections. No other peaks, including diffraction peaks from the Si substrate, were observed.

A.3. DISCUSSION

The presence of CoSi_2 diffraction peaks in this film clearly demonstrates that the deposition of 700 $\text{\AA}$ of Co on Si(111) followed by annealing forms CoSi_2 . The lack of any additional diffraction peaks indicates that no other crystalline Co-containing phases such as Co, Co_2Si , or CoSi are present.

The intensity of the (111) CoSi_2 peak observed is much greater than would be expected from a randomly oriented CoSi_2 powder sample and suggests that CoSi_2 grows on Si(111) with a preferred (111) orientation. This, of course, is consistent with the epitaxial growth of $\text{CoSi}_2(111)$ on atomically clean Si(111) substrates. The preferred orientation is also consistent with the

faint hexagonal LEED pattern observed from this film, if one assumes that the LEED pattern is from CoSi_2 and not from regions of bare Si between CoSi_2 islands. The presence of CoSi_2 diffraction peaks other than the (111) peak indicates that the CoSi_2 is not an epitaxial, single crystal film. A CoSi_2 film grown on an atomically clean Si(111) substrate would be expected to give better epitaxy and an even stronger (111) CoSi_2 reflection. The detrimental effect of interfacial oxygen and nitrogen on the epitaxial quality of CoSi_2 films grown on Si(111) was observed in Chapter 3 using LEED. The decrease in epitaxial quality of CoSi_2 films grown on Si under non-UHV conditions has also been reported by Tung and coworkers, who characterized the single-crystalline quality of CoSi_2 films with RBS by detecting the backscattering of He nuclei that were directed down the open $\langle 110 \rangle$ and $\langle 114 \rangle$ channels of CoSi_2 films.⁸

The lack of a Si(111) diffraction peak is due to the single-crystalline nature of the Si(111) wafer: unless the angle between the incident X-ray beam and the Si wafer is identical to that between the Si wafer and the detector, no diffraction peaks will be observed. Since these two angles could not be changed individually on the diffractometer used, fulfillment of the diffraction condition for the Si(111) reflection required careful mounting of the sample. Si(111) reflections were not seen in any diffraction patterns.

One sample was prepared under UHV conditions by depositing 130 Å of Co onto an atomically clean Si(111) substrate and annealing to 700°C. The evolution of the surface composition as a function of temperature showed

the same sequence of phases formed (Co_2Si , CoSi , CoSi_2) reported for 35 Å and 15 Å Co films in Chapter 3. The LEED pattern of this film showed a 7×7 reconstruction, possibly caused by islanding of CoSi_2 on the $\text{Si}(111)$ substrate. The X-ray diffraction pattern of this film showed only extremely weak peaks at angles corresponding the (111) diffraction of Si and CoSi_2 . It is believed that the epitaxial quality of this UHV-grown $\text{CoSi}_2(111)$ film was much higher than that of the previous, thicker CoSi_2 film grown on an oxidized $\text{Si}(111)$ substrate. Just as in the case of diffraction from a single-crystalline $\text{Si}(111)$ substrate, the higher epitaxial quality of this $\text{CoSi}_2(111)$ film required exact sample mounting to satisfy the diffraction conditions and observe the (111) diffraction peak. It is expected that a diffractometer permitting rotation of the sample stage independently of the source and detector would enable observation of the (111) diffraction peaks of epitaxial $\text{CoSi}_2(111)$ films and of the $\text{Si}(111)$ substrate.

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X-Ray Diffraction of Thick Film

CoSi₂(111)

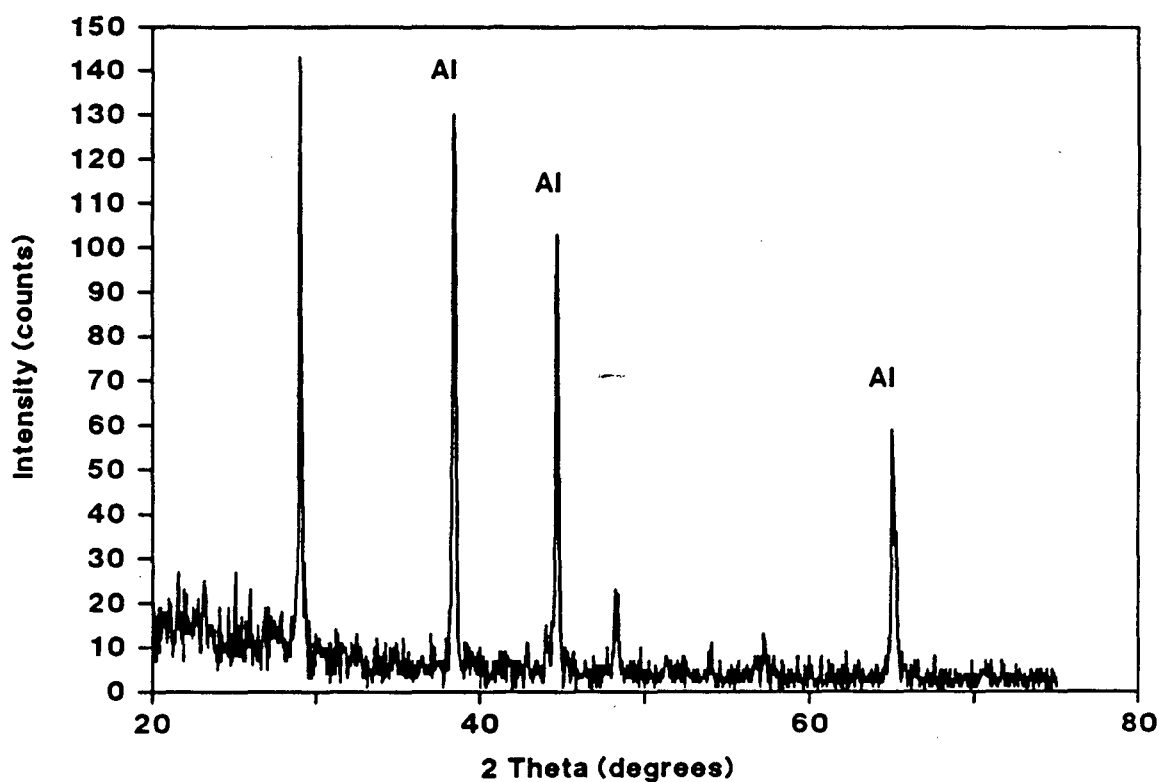


Figure A.1. The X-ray diffraction pattern of a CoSi₂ film, grown by depositing a 700 Å Co film on a Si(111) substrate under non-UHV conditions. The Al diffraction peaks are due to the aluminum sample holder.

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