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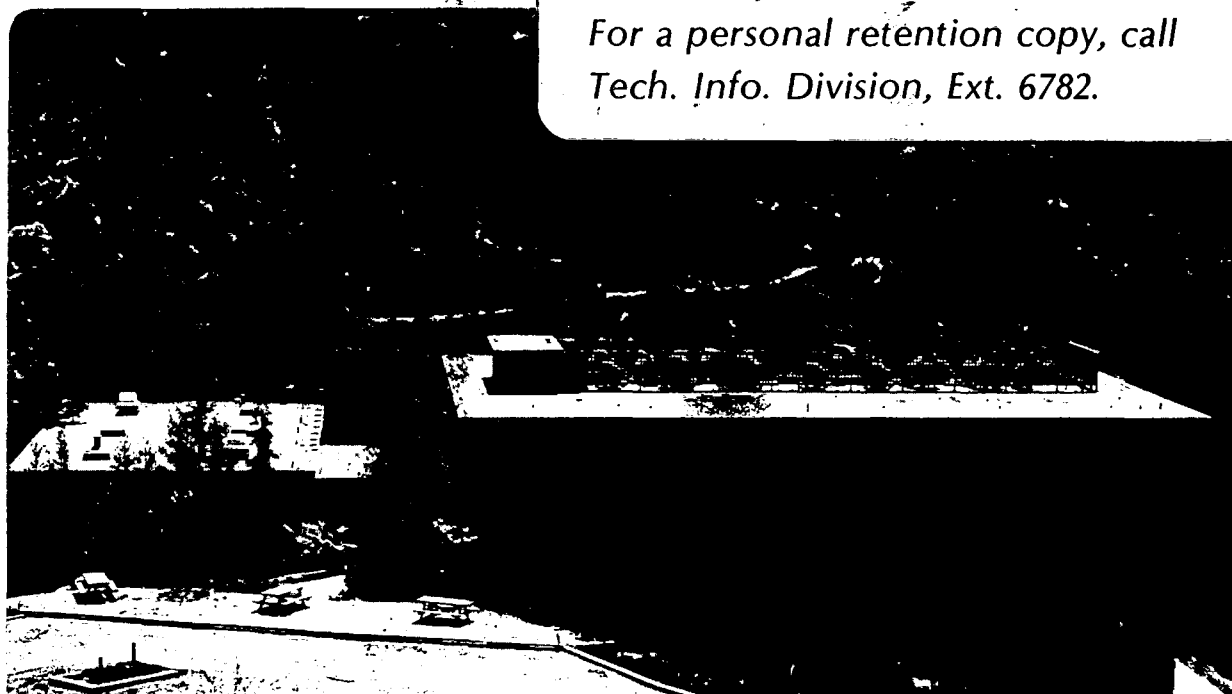
STRUCTURAL AND PHOTOELECTROCHEMICAL PROPERTIES
OF PLASMA DEPOSITED TITANIUM DIOXIDE

Larry McClease Williams
(Ph.D. thesis)

September 1982

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Berkeley, CA 94720

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ABSTRACT

A glow discharge was used to enhance the reaction rate between titanium tetrachloride and oxygen to deposit thin films of titanium dioxide. Structural, optical, electronic, and photoelectrochemical properties of the films were examined as functions of deposition parameters: temperature (ambient to 700 degrees C), substrate material (Si, sapphire, glass, quartz, NaCl, and Ti), and radio frequency power (5 to 200 watts).

Film structure was studied with x-ray diffraction, SEM, and TEM. Films deposited onto glass substrates were amorphous for temperatures less than 300 degrees C, anatase at 300 and 400 degrees C, a mixture of anatase and rutile at 500 degrees C, and only rutile at 600 degrees C and above. Films deposited on the other substrates showed similar behavior, but the temperatures differed for each substrate. The largest crystallites were obtained using low rf powers (5 to 10 watts) and sapphire substrates.

ESCA and AES showed chlorine present in films deposited at 200 degrees C and below. Chlorine was undetectable in films deposited at or above 400 degrees C. The presence of

chlorine in the films affected the electronic properties by acting as an electron acceptor. Dielectric constants for the films ranged from 25 to 166.

Plasma deposited titanium dioxide photoanodes were fabricated with quantum efficiencies of 60 to 80 % for the photoelectrolysis of water. Deposited anodes had higher quantum efficiencies than thermally grown anodes prepared in this study. The high long - wavelength photoresponse for the deposited films resulted from their large, well - oriented grain structure. Chlorine exposure of the deposited films during the deposition may have contributed to the superior short - wavelength photoresponse. This is supported by the observed increase in short wavelength photoresponse for the thermally grown photoanodes after being annealed in a chlorine - helium mixture.

James W. Hiss

TO MY MOTHER

ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

1.1 Titanium Dioxide Thin Films

Titanium dioxide has a number of unusual properties which make it suitable for a variety of thin film applications (1-5,9,10,11). Its high optical transmittance, high refractive index, and chemical stability are attractive features for optical coatings (3,4,5,10). Due to its unusually high dielectric constant, titanium dioxide thin films have been investigated for use in fabricating capacitors in microelectronic devices (2,11). Titanium dioxide has also been found capable of supporting the photoelectrolysis of water and thus has been investigated for possible solar energy conversion schemes (6,12-23).

For the above applications, films of titanium dioxide have been made by techniques such as oxidation of titanium (6,10), sputter deposition (9,49), chemical vapor deposition (1,3,4), and vacuum evaporation (2). These methods usually do not offer much versatility in selecting and controlling the properties of the films. For instance, oxidation requires high temperatures and titanium substrates. Chemical vapor deposition (CVD) also requires high temperatures to react titanium tetrachloride and oxygen. Lower temperatures can be used if water vapor is used as the oxidant and if an organo - titanium compound is used instead of the halide (27,28). These reactions, however, may cause carbon and / or hydrogen incorporation into the films which

can alter the electronic properties (29-31). Sputter - deposition and evaporation require expensive vacuum systems (131).

Plasma enhanced deposition offers far more freedom in selecting deposition conditions than do the methods indicated above. Thus, by using plasma enhanced deposition, it should be possible to "tailor" the properties of titanium dioxide films for specific applications. Some studies have been performed in which titanium dioxide was deposited using plasma enhanced deposition (7,8), but very little information on the properties of the films has been reported. As a result of this situation, the present study was undertaken to deposit thin films of titanium dioxide by using a plasma to kinetically enhance the reaction between titanium tetrachloride and oxygen. The structural, optical, electrical, and photoelectrochemical properties of plasma deposited titanium dioxide were investigated as functions of deposition parameters.

1.2 Properties Of Titanium Dioxide

The properties of titanium dioxide have been extensively studied (24-28,32-42). General reviews of the properties were presented by Grant (32) up to about 1959 and by Clark (27) up to 1968. Most of the other studies concentrated on particular types of properties. For instance, structural properties and phase transition properties of titanium dioxide have been reviewed by Rao et

al. (42); phase diagrams and x-ray diffraction properties (39-42) have also been published for the titanium - oxygen system. Electrical conductivity, dielectric constant (24,32,33,34,37), solid junction photoelectronic properties (35,36,38), and photoelectrochemical properties (12-23) have also been reviewed.

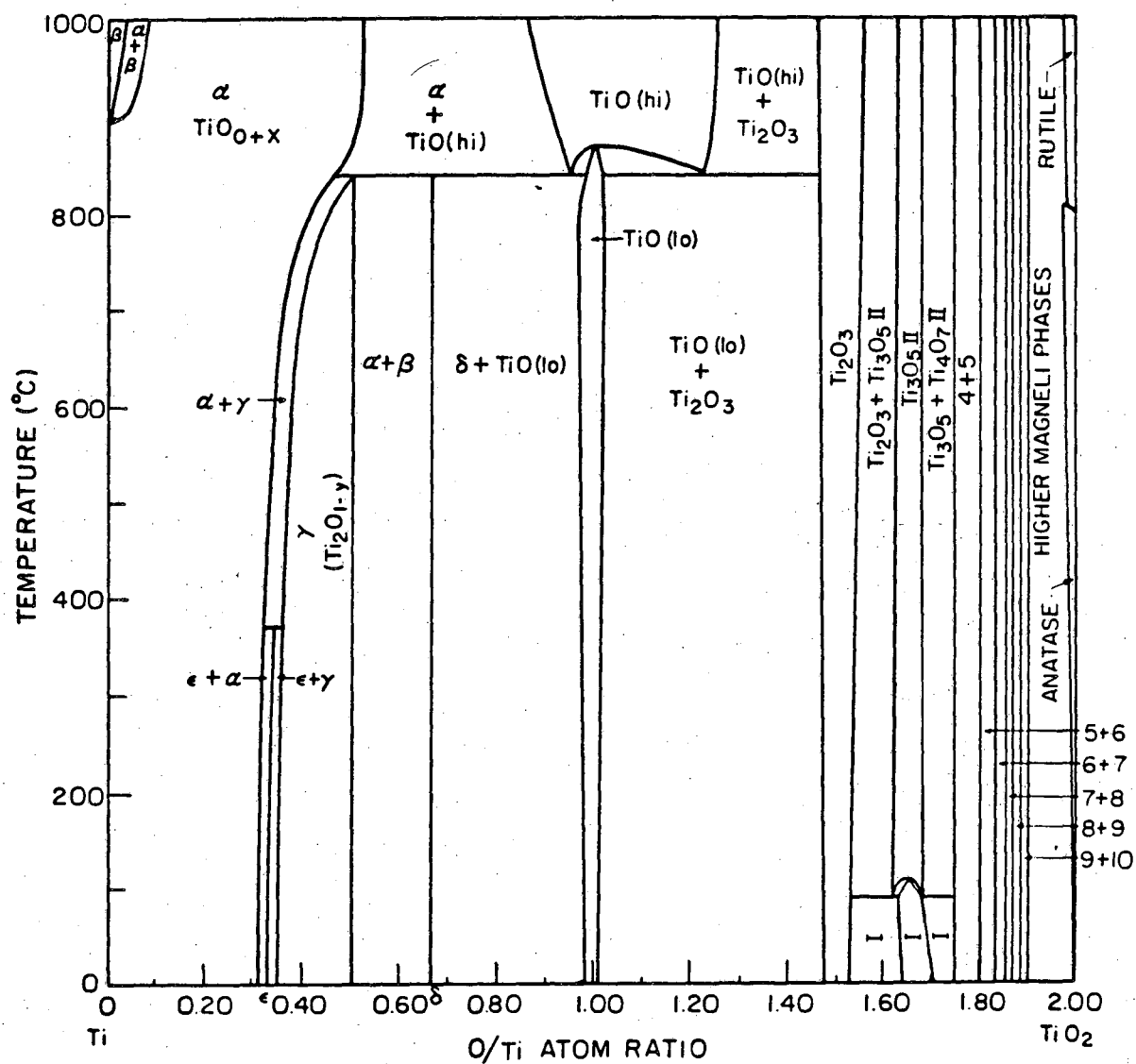
1.2.1 Structural Properties

Titanium dioxide can exist in either of three crystalline phases: brookite, anatase, and rutile. Brookite, the orthorhombic form, is difficult to make and requires the presence of sodium ions (27). Anatase can be formed, at suitable temperatures, during the oxidation of titanium compounds (27,28) or by heating amorphous titanium dioxide (27,28). Both anatase and brookite are thermodynamically less stable than the rutile modification and heating them above approximately 800 C (i.e. the C denotes degrees C) converts them to rutile (27). Anatase and rutile have tetragonal structures; the lattice parameters for the three phases are summarized in Table 1 along with other important properties. Figure 1 shows the phase diagram for the titanium - oxygen system and Figure 2 illustrates the crystal structures for anatase and rutile.

Thin films of titanium dioxide have been deposited by a wide variety of techniques. Structural properties of the films are largely determined by the deposition conditions. There have been few reports on the structural properties of

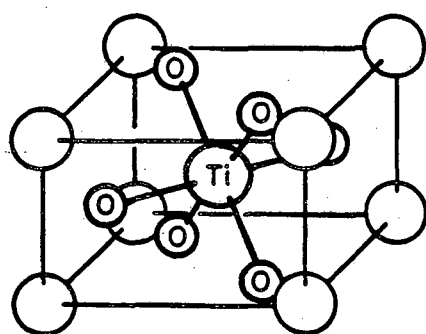
Table 1. Important Properties For Titanium Dioxide

	Brookite	Anatase	Rutile	Ref.
Density (g/cm)	4.13	3.90	4.27	(27)
Structure	ortho-rhombic	tetragonal	tetragonal	(27)
Lattice constant (A)				
a	9.15	5.36	4.59	
b	5.44			
c	5.14	9.53	2.96	
Refractive Index		2.56 2.49	2.61 2.90	(27)
Dielectric Constant	78	48	110-117 ave. 180 c-axis 89 a-axis	
Resistivity (ohm-cm)			1.0 E 14	(27)
Electron Mobility (sq cm/volt sec)			1.0	(24)

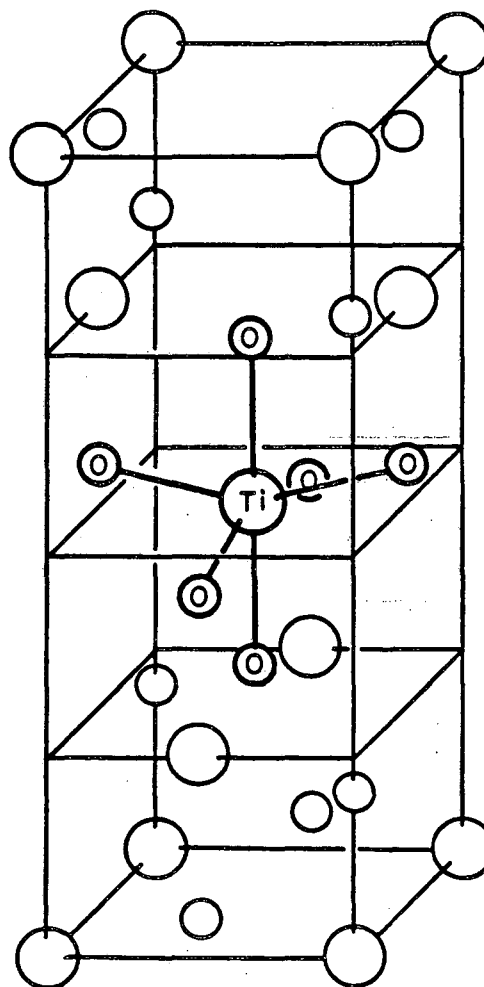


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Fig. 1. Phase diagram: titanium oxygen system (9).



RUTILE



ANATASE

XBL828-4012

Fig. 2. Lattice structures for anatase and rutile (27).

titanium dioxide films deposited in plasmas. However, there have been several studies of the structural properties of titanium dioxide films made by CVD. One of the most extensive studies was by Ghoshtagore et al. (88). The films were deposited onto a variety of substrates, including silicon and sapphire, by reacting titanium tetrachloride and oxygen. In all cases, the films were rutile over the temperature range of 400 to 1050 C. The maximum crystallite dimensions for films deposited at 700 C onto silicon substrates was 147 nm. Epitaxial (single crystal) titanium dioxide films were obtained on sapphire substrates at temperatures between 827 and 927 C.

Harbison (89) and Hass (10) examined the structural properties of titanium dioxide chemical vapor deposited from titanium tetrachloride and water vapor. Hass (10) used glass and rocksalt substrates at deposition temperatures of 200 and 300 C. The films were amorphous for deposition temperatures below 280 C. After annealing the films at temperatures above 300 C, they became anatase. All films deposited at 300 C were anatase; heating those films above 900 C converted them to rutile. The same titanium dioxide film structures were obtained for glass substrates and rocksalt substrate.

Some structural information has also been reported for titanium dioxide films deposited using water vapor and organometallic titanium compounds (3,11,90). The films deposited at 150 C were amorphous. These films could be

converted to anatase after annealing at 350 C, to a mixture of anatase and rutile after annealing at 700 C, and to pure rutile after annealing at 1000 C (3). Mollers et al. (91) deposited films at 450 C and found that they were polycrystalline with grains sizes less than 100 nm. Yokozawa (92) obtained amorphous films or anatase for deposition temperatures ranging from 320 to 750 C.

1.2.2 Electronic And Optical Properties

Of the three phases, rutile has probably been the most extensively studied. Rutile also has the most attractive properties for many of the electronic and optical applications.

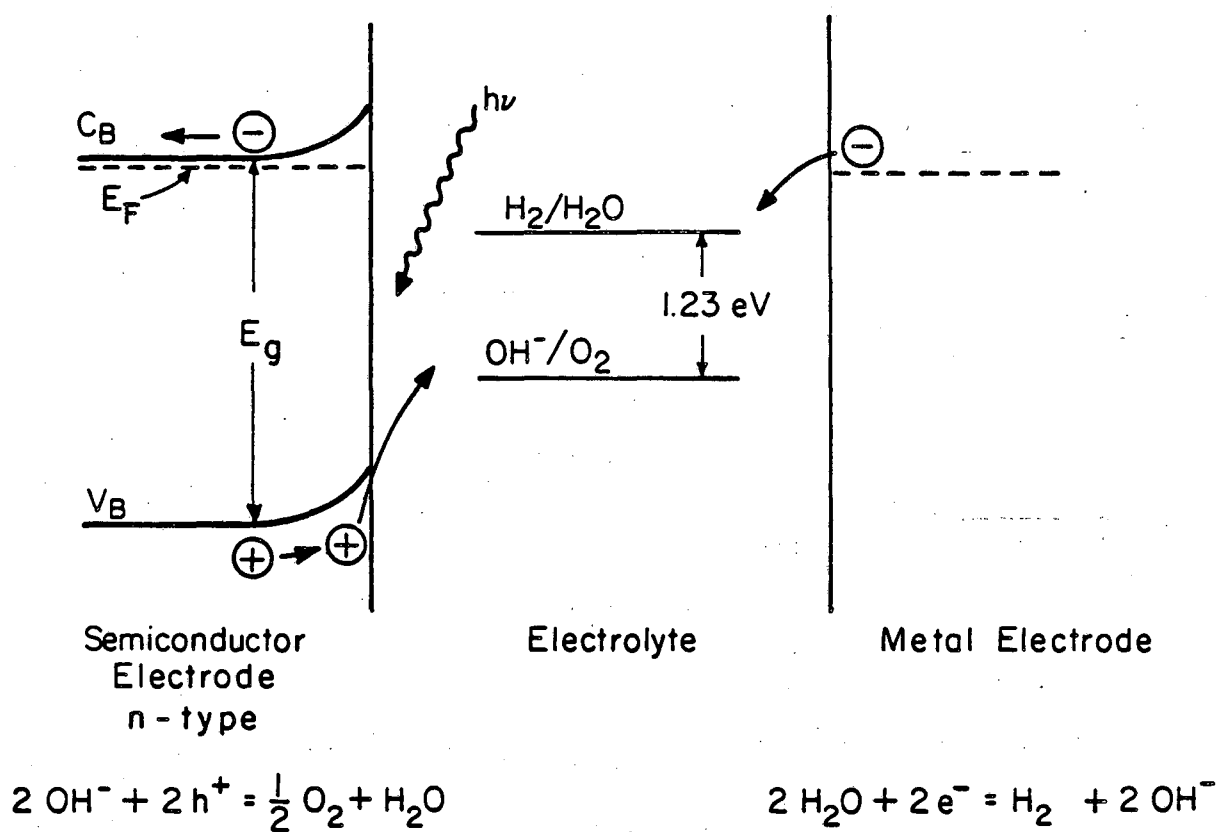
Basically, titanium dioxide is a semiconductor with a bandgap of 3.0 eV (27) and if it is undoped it can have a resistivity of 1.0×10^{14} ohm-cm (i.e. the E denotes scientific notation; times 10 to the power of 14) at room temperature. If oxygen vacancies are present, then titanium dioxide shows n-type conductivity with electron mobilities of 1 sq cm/volt sec for single crystal rutile and 0.1 sq cm/volt sec for polycrystalline rutile (24). The dielectric constant for titanium dioxide is very high and depends on crystal orientation. Thus, single crystal rutile can have a dielectric constant ranging from 89 to 180 (27). Table 1 summarizes some of the electronic properties for all three crystalline forms of titanium dioxide.

1.3 Photoelectrochemistry: Basic Principles

Photoelectrochemistry involves the use of light to drive or help to drive electrochemical reactions. For the present study, the main area of interest is in driving the water electrolysis reaction using a metal electrode and a semiconductor electrode, which serves as the photoelectrode. Titanium dioxide, an n-type semiconductor, is used as a photoanode; oxygen is generated at its surface while hydrogen is generated at a platinum electrode.

The key to effecting photoelectrolysis lies in the nature of the semiconductor - electrolyte interface. This interface has been extensively described in the literature (13,20,61,63); the actual phenomena involved are complex, but the basic concepts can be described with an idealized model. Figure 3 illustrates the important interfaces for photoelectrochemistry. When an n-type semiconductor is immersed in an electrolyte, the electrons near the solid surface are redistributed causing the formation of a depletion region. This redistribution results from the difference in the chemical potential for the semiconductor and the electrolyte. The depletion region width continues to grow until the chemical potentials for the two media become equal (19,20). The Fermi energy, (the electron chemical potential in the semiconductor), is lowered and causes the conduction band and valence band to bend upward, as shown in Figure 3. A potential barrier against further

Semiconductor Electrolyte Junction



XBL818-6381

Fig. 3. Semiconductor electrolyte junction.

charge transfer is thereby formed (20). This junction between the semiconductor and the electrolyte has electronic properties very similar to those for the Schottky barrier, semiconductor - metal interface (13,14,19,20). In fact, the semiconductor - electrolyte interface is often modeled as a Schottky barrier (123-126).

Illumination of the semiconductor - electrolyte junction with light of energies greater than or equal to the bandgap of the semiconductor promotes electrons from the valence band to the conduction band. As a result of the charge carrier generation, the Fermi level is raised thereby reducing the band bending and providing a driving force for carrier transfer between the electrodes and the electrolyte (20). In the ideal case, the band bending under illumination is sufficient to allow separation of the photogenerated electron-hole pairs; if not, an external potential must be applied. The electric field, created by the depletion region, pushes the photogenerated holes to the surface of the semiconductor where they accept electrons from the hydroxide ions (for basic electrolytes) and generate oxygen according to the reaction:



Simultaneously, the photogenerated electrons are pushed toward the bulk of the semiconductor, diffuse to the backside of the semiconductor, and are transported by a wire

to the metal electrode. At the surface of the metal electrode, the electrons then react with the water molecules to yield hydrogen according to the reaction:



The net reaction is:



whereby the n-type semiconductor is a photoanode and the metal electrode is the cathode. Ideally, all of the energy for driving the reaction can be supplied by the light.

Photoelectrodes can also be fabricated using p-type semiconductors, whereby the semiconductor would serve as a photocathode. The same basic phenomena occur as for the n-type anodes except the direction of movement for the charge carriers is reversed and the semiconductor energy bands bend downward.

1.3.1 Problems With Present Photoelectrochemical Technology

Photoelectrochemistry is a reasonably simple method by which sunlight can be used to synthesize desired chemical products for fuel or other applications. However, present day photoelectrochemical technology is unsuitable for solar energy applications because of the following problems: (a) the semiconductors with bandgaps suitable for solar energy

conversion are subject to rapid corrosion during the photoelectrochemical process, (b) stable semiconductors have bandgaps that are too large for absorbing sunlight, (c) stable semiconductors with reasonable bandgaps require a large bias voltage for operation (14,18). In addition, photoelectrochemistry suffers from many of the same problems encountered with other solar energy conversion processes; i.e. the need for cheap materials and simple manufacturing methods.

Titanium dioxide is one of the semiconductors that remains chemically stable during the photoelectrolysis of water, but its band gap (3.0 eV) is too large to absorb a significant fraction of the solar spectrum. Only wavelengths less than about 420 nm (51) are absorbed.

1.4 Photoelectrochemistry: Previous Work

Photoelectrochemistry has been a topic of scientific investigation for well over a hundred years. However, most of the work done on photoelectrochemistry was started after 1969 when Fujishima et al. (12) showed that titanium dioxide could sustain the photoelectrolysis of water and remain stable. Since then, there have been numerous studies on the photoelectrochemical properties of titanium dioxide and other materials. Several excellent review papers (13-23) covering the work done up to about 1980 are available.

A survey of the literature shows that large differences exist in the experimental conditions used to measure the

photoelectrochemical properties of titanium dioxide. Quite often, the photoresponse is reported as the photocurrent density. In this form, the results cannot be used for comparison with the results of other investigators unless the light sources are equivalent in intensity and spectrum. To help avoid this problem, the results should be reported as quantum efficiencies. By definition, the quantum efficiency is equal to the photocurrent density divided by the light flux.

Rather than present a general review of photoelectrochemistry, only those reports that are related to the present study are discussed. These have been divided into the following areas: thin film titanium dioxide used for the photoelectrolysis of water, plasma related deposition techniques used for making the titanium dioxide photoanodes, and efforts to improve the photoresponse of titanium dioxide.

1.4.1 Thin Film Titanium Dioxide Photoanodes

Thin film titanium dioxide photoanodes have been made by a variety of techniques. All thin film photoanodes made to date have been polycrystalline or amorphous; consequently, the films usually have a lower photoresponse than that for the single crystal anodes. However, Fujishima et al. (43) and Mavorides et al. (6) thermally oxidized titanium substrates to form titanium dioxide films for photoelectrodes and found that the polycrystalline anodes

worked almost as well as the single crystal electrodes. Other investigators have also studied the photoelectrochemical properties of thermally grown titanium dioxide thin film photoanodes (44-47).

Chemical vapor deposition (CVD) has also been used in fabricating thin film titanium dioxide photoanodes. Hardee et al. (90) deposited titanium dioxide films onto titanium substrates at 150 C by reacting tetra-isopropyl ortho-titanate with water vapor. To prevent the films from cracking, 400-500 nm was deposited and then annealed in a bunsen burner for 3-4 minutes. The process was subsequently repeated to obtain the desired film thickness. At the end of the deposition process, the conductivity was further increased by a 600 C reduction in vacuum (10 microtorr). Comparison of the deposited films to single crystal rutile indicated that the photocurrent properties of the single crystal anodes were a factor of 2 to 4 times higher than the CVD anodes.

Mollers et al. (91) deposited titanium dioxide films onto titanium sheet metal and onto conducting tin oxide at 450 C by air oxidation of titanium acetylacetonate. Their films were polycrystalline with a grain size less than 0.1 micron. When illuminating the electrode from the titanium dioxide - electrolyte interface (front side) they found that the magnitude of the photocurrent in the photocurrent - wavelength response depended on the thickness of the film; as the thickness decreased, the peak current increased but

also shifted to shorter wavelengths. However, illuminating the electrode from the tin oxide - titanium dioxide interface (backside) showed no thickness variation in the wavelength at which the photocurrent was a maximum. It seemed that the distance the electrons had to travel to reach the back contact was the limiting factor; as a result, they claimed that electrons were more readily trapped than holes.

Stalder et al. (53) formed thin films of titanium dioxide on titanium substrates by decomposing titanium tetrachloride in air at 400-500 C. The conductivity of the films was increased by heating in argon for 40-60 minutes at 550-800 C. Using the films as photoanodes, quantum efficiencies of 0.5 to 0.6 were obtained.

Polycrystalline rutile thin films were deposited by Takahashi et al. (60) onto titanium substrates by pyrolysis of ethyl titanate in oxygen at 400-500 C. The only post-deposition treatment the films received was a 10 second anneal in a bunsen burner. These photoanodes had quantum efficiencies in the 0.7 to 0.8 range and were comparable to single crystal rutile photoanodes.

1.4.2 Titanium Dioxide Photoanodes Fabricated By Sputtering And Arc Plasma Techniques

Only two studies in which titanium dioxide photoanodes were fabricated by methods "related" to plasma enhanced deposition have been reported. In one of the studies (48),

rutile powder was arc-plasma sprayed onto substrates to form thin films of rutile. The photoanodes behaved similarly to other polycrystalline titanium dioxide electrodes.

Soliman et al. (49) made thin film titanium dioxide photoanodes by reactive sputter deposition using oxygen and a titanium target. The photoanodes were polycrystalline and had a low photoresponse. The authors state that reactive sputtering is attractive for fabricating thin film photoelectrodes because of the versatility and ease with which the composition and electrical properties can be varied.

1.4.3 Efforts To Improve The Photoelectrochemical Properties of Titanium Dioxide

Table 2 lists some of the elements that have been added to titanium dioxide in an effort to improve the photoelectrochemical properties. The plus (+) indicates that the photoanodes containing the added element had higher photoresponse than the anodes containing only oxygen and titanium. The minus (-) indicates there was no improvement in the photoresponse for the anodes containing the added element over that for the pure anodes. The purpose for most of the investigations was to increase the visible light sensitivity of the titanium dioxide by introducing a new energy level within the bandgap (50,52-54,58). Thus, ideally, electrons could be excited to the new energy level with photons of lower energy than is required for pure

Table 2. Elements Added To Titanium Dioxide Photoanodes

Element	Effect (+ good, - bad)	References
Aluminum	+ +	51,54
Beryllium	+	52
Boron	+	54
Cadmium	+	52
Chromium	+ -	51,52
Cobalt	+	55
Europium	+	54
Fluorine	+	57
Gallium	+	54
Iron	-	56
Nickel	-	52
Niobium	+	50
Strontium	+	54
Tungsten	-	59
Zinc	-	52

titanium dioxide. Generally, it was found that in cases where the spectral range was extended, the magnitude of the quantum efficiency over the entire range was reduced (52,55,58) or a higher bias potential was required for the photocurrent onset (51,56,58). In instances where the element addition increased the photocurrent, the most probable explanation is that the photoanodes containing the new element had a lower recombination rate than the pure titanium dioxide (51,52,54,57). This is mainly supported by the fact that the wavelength range for the photoresponse was unchanged by the element addition.

1.5 Plasma Enhanced Deposition

Plasma enhanced deposition is receiving a great deal of attention for use in numerous thin film applications (63-66). The primary advantage of this technique is the ability of high energy electrons (0.5-10.0 eV) in the plasma to break chemical bonds. In this way, chemical reactions that otherwise require high temperatures to proceed at a reasonable rate can be promoted by glow discharges at low temperature (less than 300 C). Typical glow discharges for plasma deposition are generated by subjecting gases at pressures between 0.1 and 2.0 torr to large electric fields (67). Free electrons are generated in the gas and are accelerated by the action of the electric field to very high energies which correspond to electron temperatures of ten thousand to one hundred thousand K (63). Concurrently, the gas temperature is essentially unchanged and thus the low temperature gas molecules and the high temperature electrons form a nonequilibrium mixture (66,67). Collisions between the high energy electrons and gas molecules yield highly reactive species of ions, free radicals, and metastables which of course, leads to the increased reaction rates. Since the energy for the reaction is supplied by electrons, instead of by heat, almost any reaction with gaseous reactants can be made to proceed at reasonable rates while near ambient temperatures.

In addition to the versatility in promoting reactions,

plasma enhanced deposition offers many other advantages. For example, the properties of the films deposited in a plasma depend on deposition parameters such as radio frequency (rf) power density, gas pressure, frequency, gas composition, and substrate temperature. As a result, the properties of the films can be intentionally varied by changing the deposition conditions and desired properties can, ideally, be "built-into" the films. Some of the materials formed by plasma deposition are reported to have chemical and physical properties which may be unattainable by other deposition techniques (68-71).

Structural properties of thin films show a strong dependence on the deposition temperature. Since plasma deposition can drastically reduce the temperature dependence of the reaction rate, temperature becomes a free parameter for selecting the film structure; amorphous films and various polycrystalline phases can be easily obtained by varying the temperature. Plasma enhanced deposition also offers the possibility of growing single crystal films at lower temperatures than is required by other deposition methods (72-75).

Considering its ease and versatility, plasma enhanced deposition seems to be an ideal method for depositing thin films of titanium dioxide of suitable quality for many of the applications discussed earlier. The lack of previous research on plasma deposited titanium dioxide indicates that there is a need for a characterization of the process and

the properties of the resulting films in order to obtain a fuller understanding of its capabilities. The possibility of altering the optical and electronic properties of plasma deposited titanium dioxide is attractive for several applications, particularly in fabricating photoanodes.

The following goals were pursued in this study: (a) to use a glow discharge to deposit titanium dioxide thin films from titanium tetrachloride and oxygen, (b) to examine some of the basic properties of the films such as the structural, electronic, and optical properties and how they relate to the deposition parameters, (c) to examine the photoelectrochemical properties, and (d) to combine the information for (b) and (c) and use it to gain a more complete understanding of plasma enhanced deposition and its potential uses.

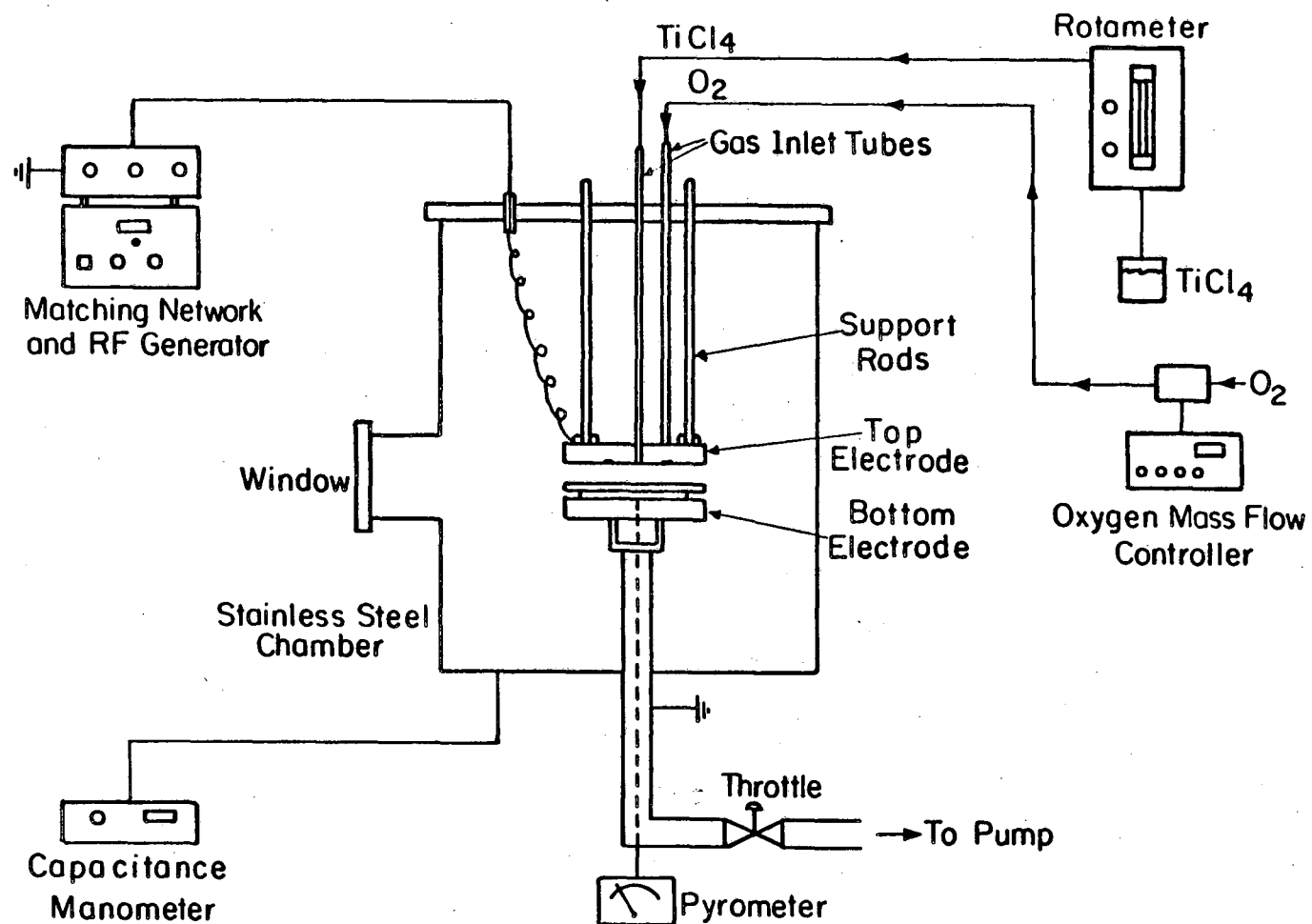
2.0 EQUIPMENT AND PROCEDURES

2.1 Deposition System

Figures 4 and 5 show the plasma deposition system utilized in this study. The reactor chamber is constructed of stainless steel and has a diameter of 25.4 cm and a height of 38.1 cm. The electrodes, also made of stainless steel, are 10.2 cm in diameter with a spacing of 1.9 cm. The reactor is fitted with a pyrex window for observation of the plasma during deposition.

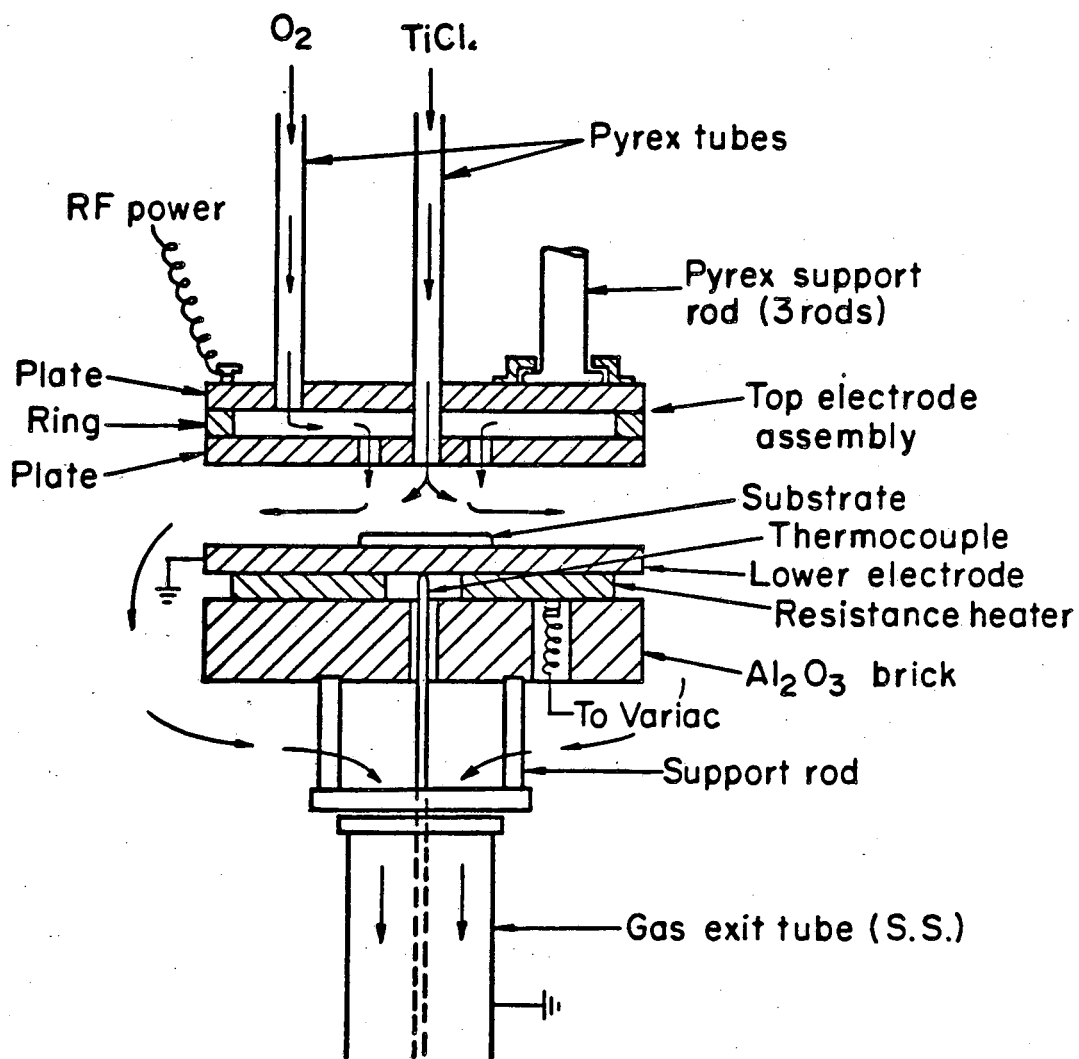
The upper electrode is suspended from the top of the reactor by three pyrex rods. As shown in Figure 5, the gas inlet tubes are connected to the top electrode, whereby the titanium tetrachloride enters the reaction zone (i.e. space between the electrodes) through the center hole (0.635 cm dia) in the electrode. Simultaneously, the oxygen enters the reaction zone through four holes (0.317 cm dia) surrounding the center hole. The lower electrode is heated with a resistance heater (Chromalox ring heater Model 135335) and is supported by a section of 99% alumina firebrick for thermal insulation purposes. A chromel - alumel thermocouple and pyrometer are used to monitor the temperature of the lower electrode (Figure 5). The lower electrode assembly is supported by the gas exit tube (3.8 cm dia) which leads to a liquid nitrogen cold trap and a corrosion resistant vacuum pump (Alcatel Model 2060C). A throttle valve (hose clamp) on the exit line is used to

Titanium Dioxide Deposition System



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Fig. 4. Plasma deposition system.



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Fig. 5. Electrode assembly for plasma deposition.

control the pumping speed (Figure 4).

Radio frequency (rf) power is applied to the top electrode using a 0-300 watt Tegal rf generator (Model RFG 300) and matching network (Model MN300) operating at 13.56 MHz. The bottom electrode is grounded. The pressure is monitored by a McLeod gauge or a capacitance manometer (MKS Baratron Gauge Model 222A). The oxygen flow rate is regulated with a mass flow controller (Tylan Model FC-260) and readout box (Model RO-14). Titanium tetrachloride (vapor pressure = 10 torr at 20 C) is stored in a glass flask maintained at room temperature by a water bath and is allowed to evaporate and enter the system as a vapor. A micrometering valve and rotameter are used for controlling the titanium tetrachloride flow rate (Fig. 62).

In a typical deposition, the lower electrode was heated to the desired temperature. The substrates were placed on the lower electrode, and the chamber evacuated to a pressure of approximately 20 mtorr. The substrates were then cleaned of organic contaminants by striking an oxygen plasma for five minutes at a pressure of 150 mtorr and the rf power selected for the deposition. At the end of the oxygen plasma treatment (descum), the titanium tetrachloride flow rate and the oxygen flow rate were set at the desired values. Using the throttling valve, the pumping speed was adjusted to give a system pressure of 150 mtorr. The plasma was activated for the desired time and the samples were removed at the end of the deposition.

Due to the various film properties to be measured, a number of different substrates were used. These substrates included glass slides, glass cover slips, quartz plates, silicon wafers (orientations were either (100) or (111)), titanium foil (Alfa Ventron 99.7% pure), sapphire wafers (1-102), or sodium chloride (Barnes Analytical). Before being placed in the reaction chamber, the titanium foil was etched in a dilute (approximately 2%) hydrofluoric acid solution and then rinsed in deionized water.

2.2 Thickness Measurement

For some of the glass slides, the film thickness was estimated using microbalance techniques. Knowledge of the weight of the film, the area, and the density allowed calculation of the thickness. The weight measurements were made on a microbalance (Mettler Instruments Corp. Type M5). A density of 3.9 g/cc was used for these calculations. These measurements were used only for determination of the activation energy for deposition; therefore, exact thickness measurements are unnecessary -- activation energy is based on relative reaction rates.

Direct measurements of film thickness were also made by masking part of a silicon substrate with a section of glass slide during deposition and measuring the oxide step height using an Alpha-Step profiler (Tencor Model 10-00020). In some cases, the step was made by etching a step in the titanium dioxide using 49% hydrofluoric acid. Films

deposited at high temperatures (400 C and above) usually lifted-off the substrate rather than dissolved.

2.3 Film Structure Measurements

The x-ray diffraction properties for the films were obtained with a Picker (Model 3488) x-ray diffractometer. The x-ray source was either copper k alpha radiation (1.54 angstroms) or iron k alpha radiation (1.94 angstroms). A sodium iodide sensor was used to detect the diffracted x-rays. The intensity of the diffracted beam was recorded as a function of twice the incident angle (2 theta degrees) on a chart recorder (137).

Transmission electron micrographs and transmission electron diffraction patterns were recorded on a Siemens electron microscope using an acceleration voltage of 100 KeV.

Photographs of the film surfaces were obtained with a Hitachi scanning electron microscope (Model S-310A). To minimize charging, approximately 10 nm of gold or palladium was sputtered onto the titanium dioxide with a Hummer sputter deposition system.

2.4 Optical Property Measurements

Reflectance measurements were made on films deposited on titanium substrates (rough surface), using a Gier-Dunkle integrating sphere attachment on a Beckman DK-2 spectrometer. These measurements were done by Dr. Harold

Gurev at Optical Coatings Laboratory, Inc, Santa Rosa, California.

In addition, transmittance was measured for films deposited onto 2 mm thick quartz plates using a Perkin-Elmer spectrophotometer (Model 571, double beam, 1 nm bandpass slit).

2.5 Chemical Composition Measurements

Film compositions were analyzed using Auger Electron Spectroscopy (AES), Electron Spectroscopy for Chemical Analysis (ESCA), and Secondary Ion Mass Spectroscopy (SIMS). AES measurements were performed at the Lawrence Berkeley Laboratory, while ESCA and SIMS measurements were made at the NSF Regional Facility in Surface Analysis, University of Minnesota, Minneapolis.

2.6 Electrical Property Measurements

Electrical properties of the films were measured using capacitor structures. These structures used evaporated aluminum dots (0.49 mm in radius) or a mercury probe (Materials Development Corp. Model 754, contact radius 0.381 mm) on the titanium dioxide surface. The substrates were silicon wafers or titanium foils. The titanium foils for these measurements were polished to a mirror finish with 1 micron diamond paste (Mark V Laboratory, Inc).

Capacitance-voltage (CV) properties were measured with a capacitance meter operating at 1 MHz (Boonton Electronics

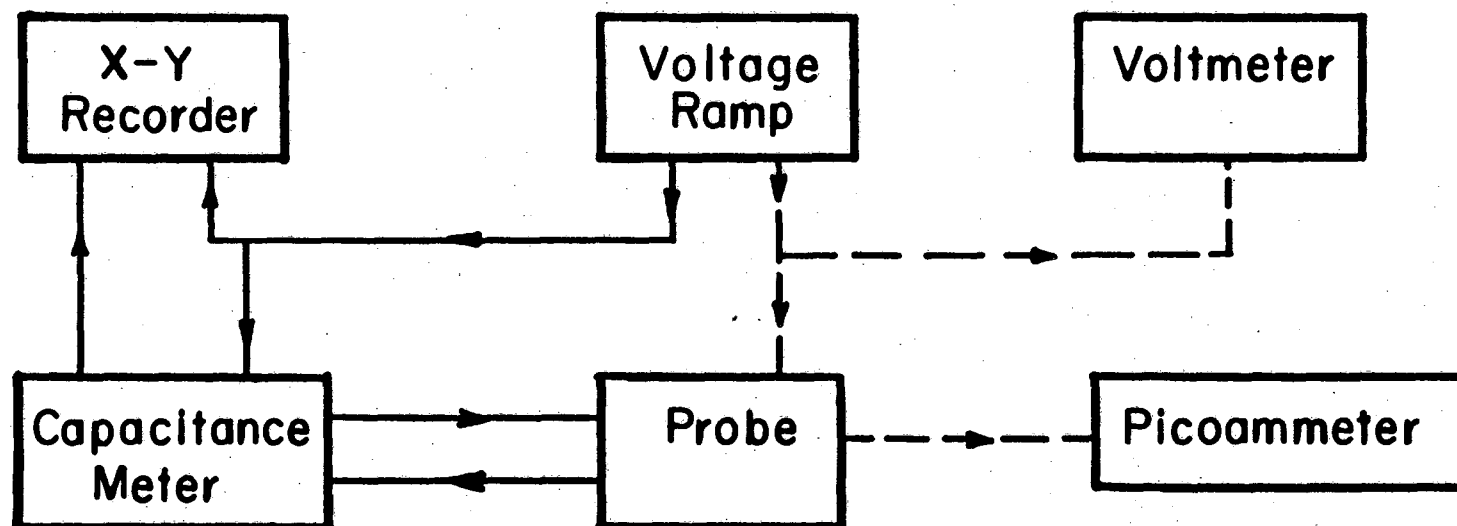
Corporation Model 71A) and a voltage ramp generator (Sample Generator 890A1) built by the College of Chemistry Electronics Shop. The CV plots were recorded on an x-y recorder (Hewlett Packard Model 7045A). The current-voltage properties were measured with a dc power supply (Sample Generator 890A1), logarithmic picoammeter (Keithley Instruments Model 26000) and a digital multimeter (Keithely Instruments Model 179). Figure 6 shows the equipment and connections for these measurements.

2.7 Anode Fabrication

A diagram of a typical photoanode used in this study is shown in Figure 7. After a titanium dioxide film was deposited onto the titanium substrate, any oxide present on the back of the substrate was scratched away. Electrical contact was then made by using silver epoxy (TRA-CON Bipax BB 2902) to attach a wire to the back of the titanium substrate. The substrate and wire were subsequently attached to a section of microscope slide with insulating epoxy (Devxon "5 Minute" Epoxy) such that only the titanium dioxide was exposed to the electrolyte.

2.8 Photoelectrochemical Equipment

The apparatus for the electrochemical measurements is illustrated in Figure 8. The electrochemical cell was an ultraviolet - absorbing polyacrylic (Polycast Technology Corporation) box with 1.25 cm thick walls. The box was



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Fig. 6. Equipment for electronic measurements.

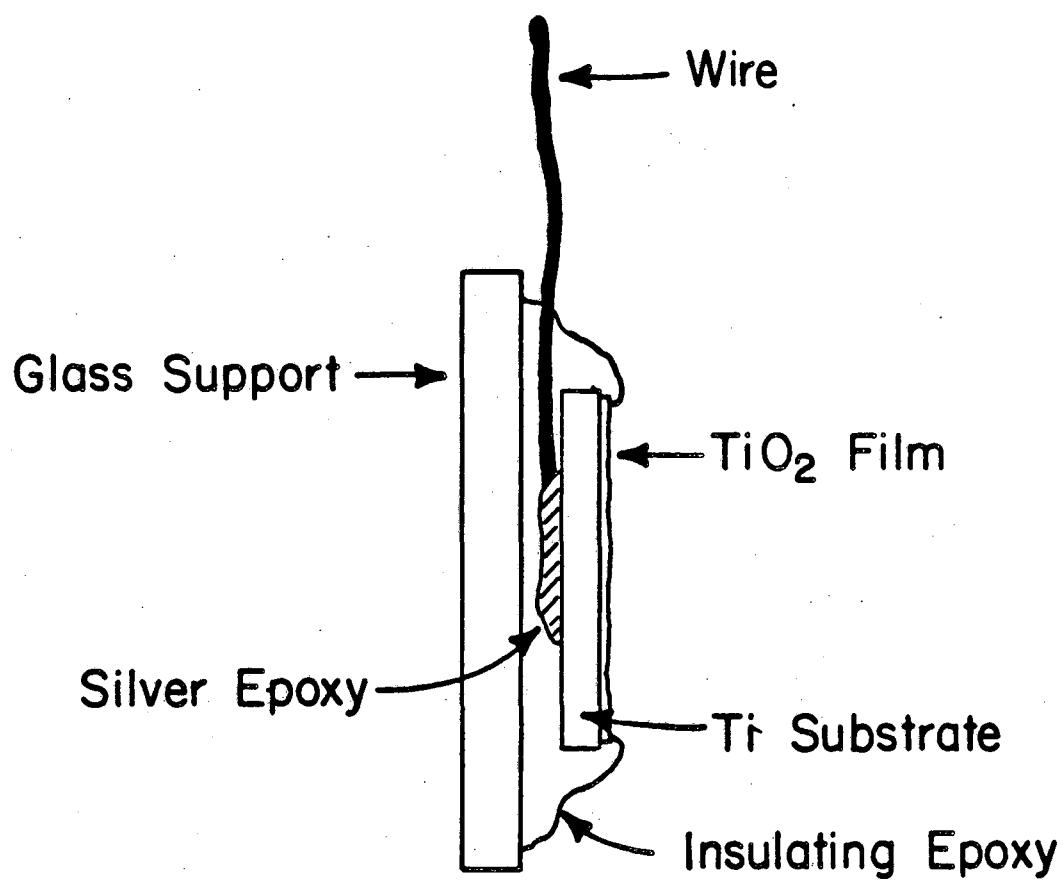
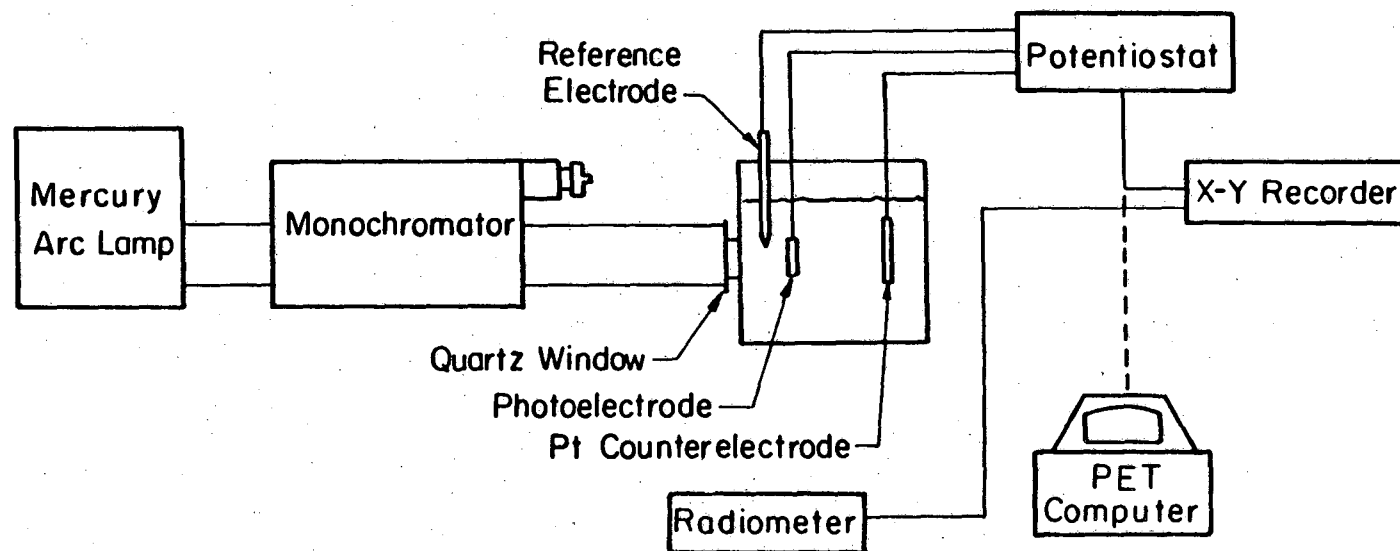


Fig. 7. Photoelectrode.



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Fig. 8. Apparatus for photoelectrochemical measurements.

fitted with a quartz window (0.32 cm thick) to allow ultraviolet light to enter. In all experiments, the electrolyte was a 1 N sodium hydroxide solution made from reagent grade sodium hydroxide and deionized water (17 megohm-cm). A saturated calomel reference electrode was located approximately 2 cm in front of the top edge of the semiconductor electrode. The photoelectrode was 4 cm from the quartz window, and the counterelectrode was a piece of shiny platinum foil (6.5 square cm). During the experiments, nitrogen was bubbled through the electrolyte to exclude air and the electrolyte was stirred with a teflon coated stirring bar.

The anode potential was controlled with a potentiostat and function generator (PAR Model 173 and Model 175 respectively) while the current was measured with a current follower (PAR Model 176). The output data were recorded on an x-y recorder (HP Model 7045A) or were read directly into a computer (Commodore PET 2001).

The light source was a 200 watt mercury arc lamp (Oriel Corporation Model 8510-4 power supply and Model 6137 housing) focused with a F/1.0 fused silica lens. A grating monochromator (Oriel Model 7240 housing and 7270 grating) with 1 nm bandpass slits was used with a wavelength scanning drive (100 nm/minute) to obtain the photocurrent- wavelength plots and lamp spectrum. The light flux from the lamp was measured with a radiometer (Optronics Laboratory, Inc Model 730A). A typical lamp spectrum is given in the Appendix.

3.0 RESULTS AND DISCUSSION

3.1 Deposition Rate and Kinetics

Appreciable reaction rates between titanium tetrachloride and oxygen can be obtained only at temperatures greater than about 600 C (76). Commercial titanium dioxide is produced at temperatures of 650-750 C by reacting titanium tetrachloride and oxygen (77,78). The activation energy for gas phase formation of titanium dioxide is reported to be 0.79 eV/atom (76). For films made by chemical vapor deposition, the activation energy is reported to be 0.78 eV/atom (79).

An Arrhenius plot for titanium dioxide films made by plasma enhanced deposition is given in Figure 9. The depositions were carried-out at 10 watts rf power, with a one to one flow ratio of titanium tetrachloride to oxygen, and with glass substrates. The deposition rate was determined by measurement of the film mass. A least squares fit of the data gave an activation energy of 0.12 eV/atom. The reduction in activation energy, brought about by using a plasma, allows higher deposition rates at lower temperatures.

According to Ghoshtagore (79), chemical vapor deposition of titanium dioxide proceeds by the Rideal-Eley mechanism; adsorbed atomic oxygen reacts with impinging titanium tetrachloride molecules from the gas phase. The

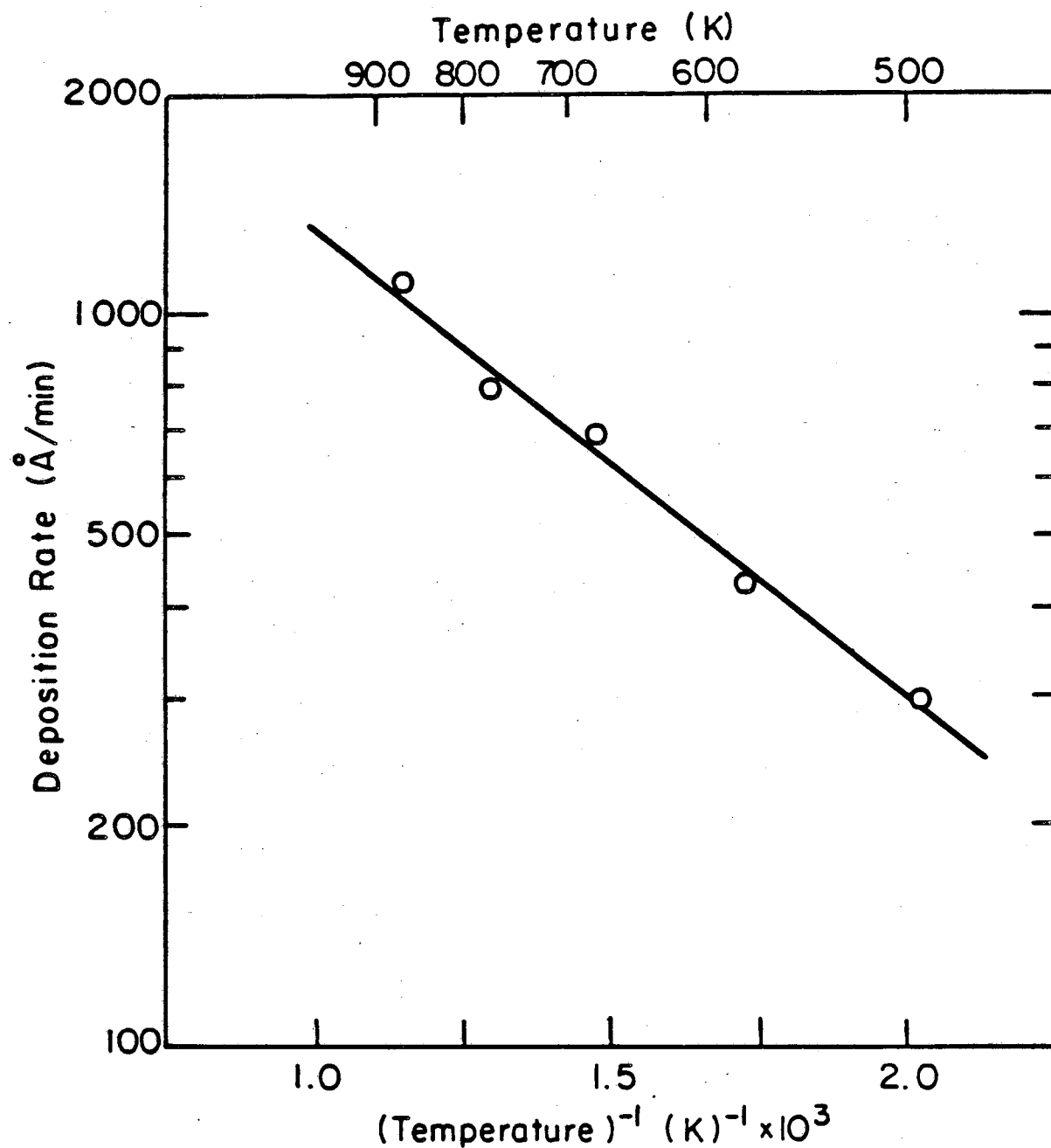


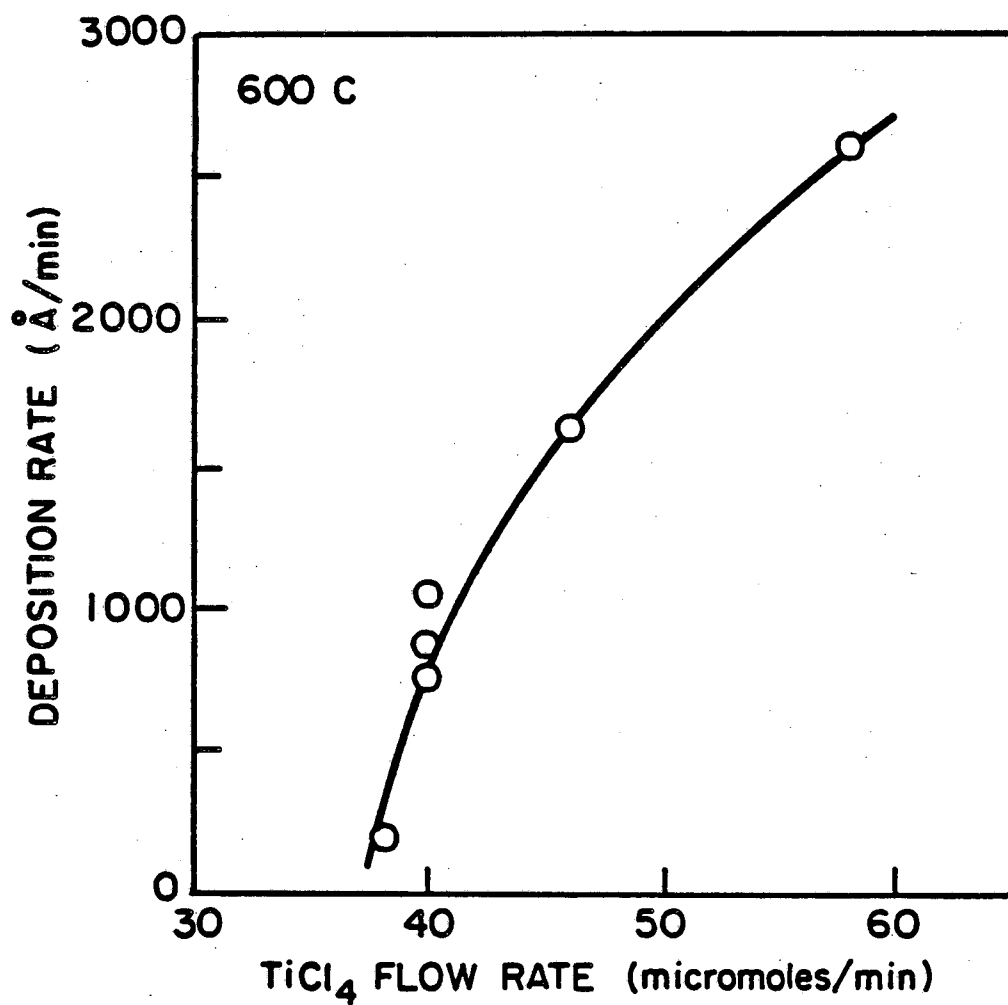
Fig. 9. Arrhenius plot for titanium dioxide plasma deposited from titanium tetrachloride and oxygen at 10 watts rf power.

high energy electrons present in a plasma enhance the reaction by generating more atomic oxygen and/or by decomposing the titanium tetrachloride into lower chlorides. Under the conditions used in this study, deposition did not occur, even at 600 C, unless a plasma was ignited. With a plasma, the deposition rate, of course, depended on all plasma deposition parameters (rf power, temperature, gas flow rates, etc). In general, the rate was usually between 100 and 3000 angstroms per minute.

The dependence of the deposition rate on the titanium tetrachloride flow rate is given in Figure 10. The deposition temperature was 600 C, and the oxygen flow rate was 45 micromoles per minute (1 sccm) for all cases. Figure 11 shows the oxygen flow rate dependence of the deposition rate for a temperature of 300 C and titanium tetrachloride flow rate of 60 micromoles per minute.

The dependence of deposition rate on rf power level is shown in Figure 12. The titanium dioxide films were deposited at 600 C, 150 mtorr, 45 micromoles of titanium tetrachloride per minute, and 360 micromoles of oxygen per minute (8 sccm). For those conditions, the deposition rate decreased as the rf power was raised from 5 to 200 watts (0.06 to 2.47 watts per square cm).

Changes in rf power input can cause numerous changes in a plasma deposition process and alter the deposition rate. For instance, the average electron energy is proportional to the plasma power (63); the electron energy is determined by



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Fig. 10. Deposition rate dependence on titanium tetrachloride flow rate.

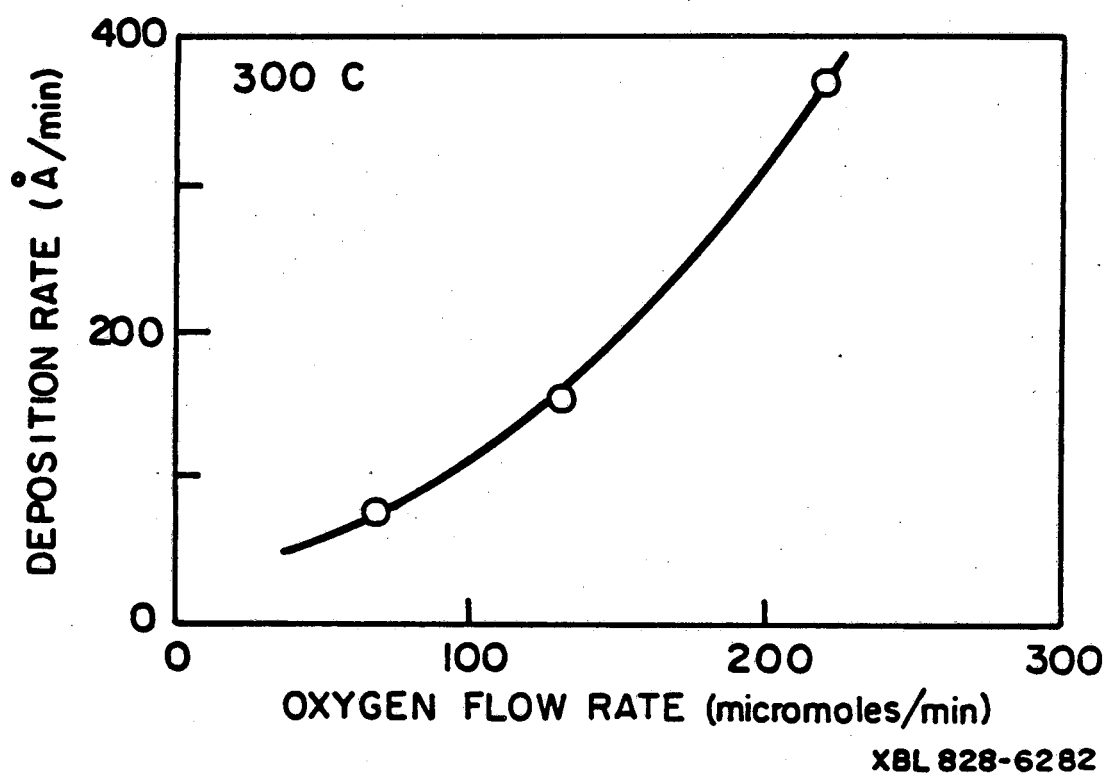
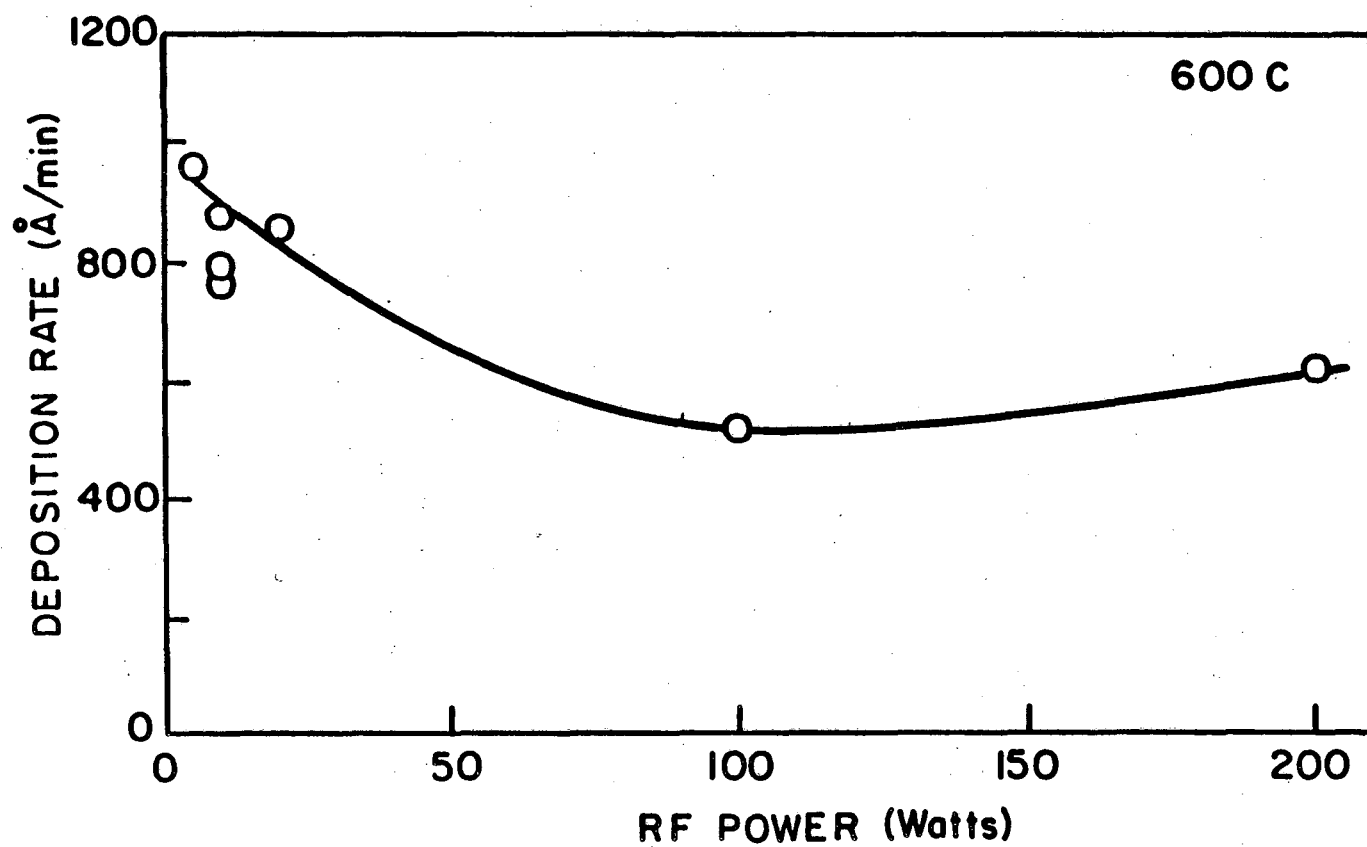


Fig. 11. Deposition rate dependence on oxygen flow rate.



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Fig. 12. Deposition rate dependence on rf power.

the local field (V/cm) and by the collision frequency (63). Ideally, a higher rf power density should give a higher deposition rate due to the increase in electron energy. However, if the presence of the higher energy electrons changes the reaction mechanism or enhances some of the competing reactions or phenomena (i.e. sputtering, desorption), the deposition rate would decrease as the rf power is raised. The increase in rf power also increases the energy of the ions bombarding the surface. At the higher power densities, competition between deposition and sputtering probably occurs, thus reducing the deposition rate. Evidence for enhanced ion bombardment is presented in Section 3.3.4.1, Film Structure.

3.2 Film Composition

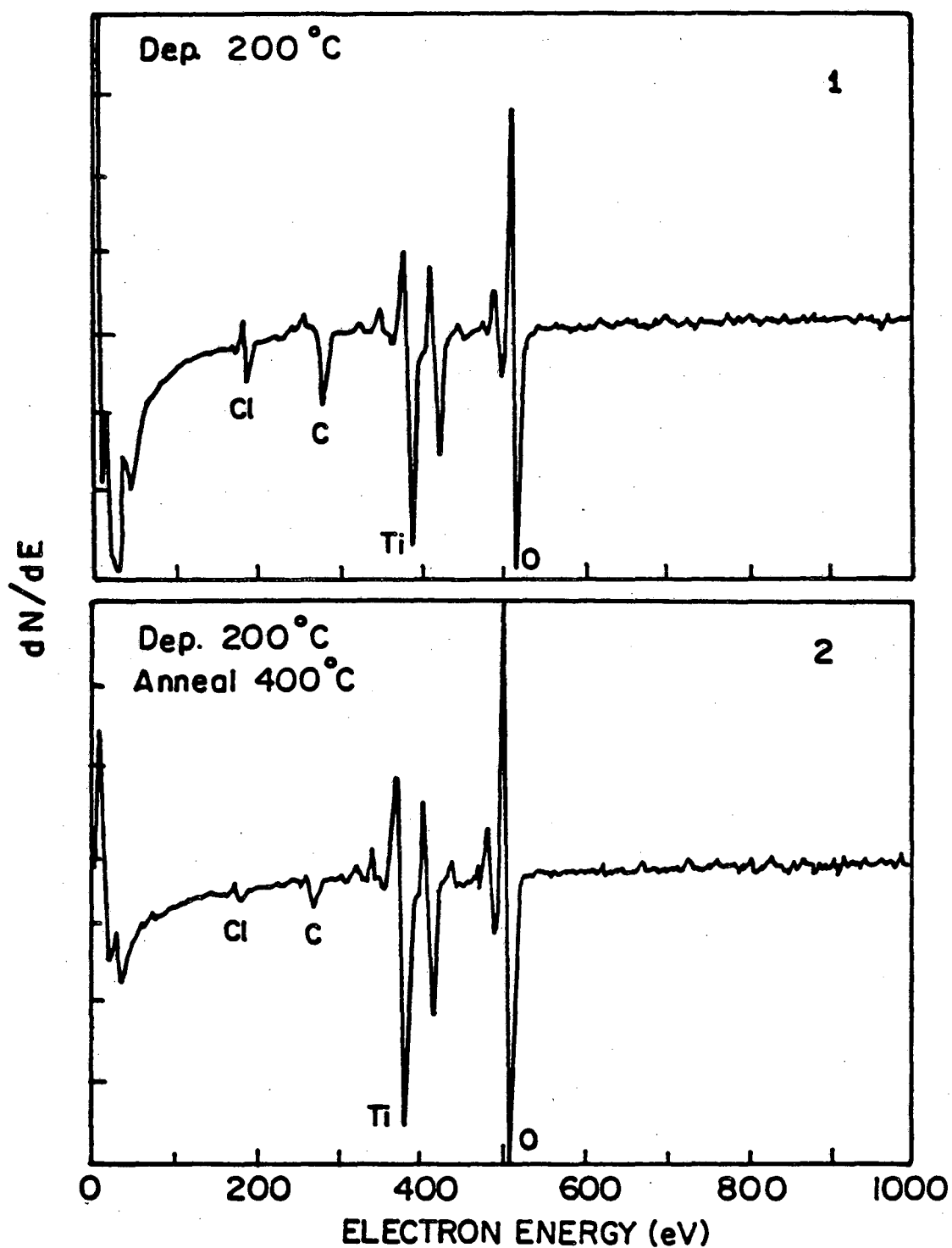
The chemical composition of a material plays an important role in establishing the material's electronic properties. Since plasma enhanced reactions can yield products with compositions unattainable by other methods, determining the composition of the plasma deposited titanium dioxide films has been an important area of interest throughout this study. In order to determine the film composition, some of the films were analyzed by Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), and secondary ion mass spectroscopy (SIMS).

Detailed descriptions of the techniques can be found in the literature (80-83). In AES, a beam of electrons is impinged upon the surface to be analyzed. As a result, electrons are ejected from the surface atoms thus creating vacancies into which other bound electrons can fall. The electrons dropping into the vacancies release energy which is then absorbed by other electrons. If the energy is high enough, then the electron can be ejected into vacuum. This electron is called the Auger electron. The energy of the Auger electron is a characteristic of the element that ejected the electron; by analyzing the energy, the element can be identified (82). ESCA involves using x-rays to eject electrons from the atoms in the material into vacuum. The kinetic energy of the electron is measured and related to

the element that emitted the electron (81,82). For SIMS analysis, a beam of high energy argon ions is used to eject atoms, molecules, and other species from the surface. The ejected particles are then analyzed with a mass spectrometer (82).

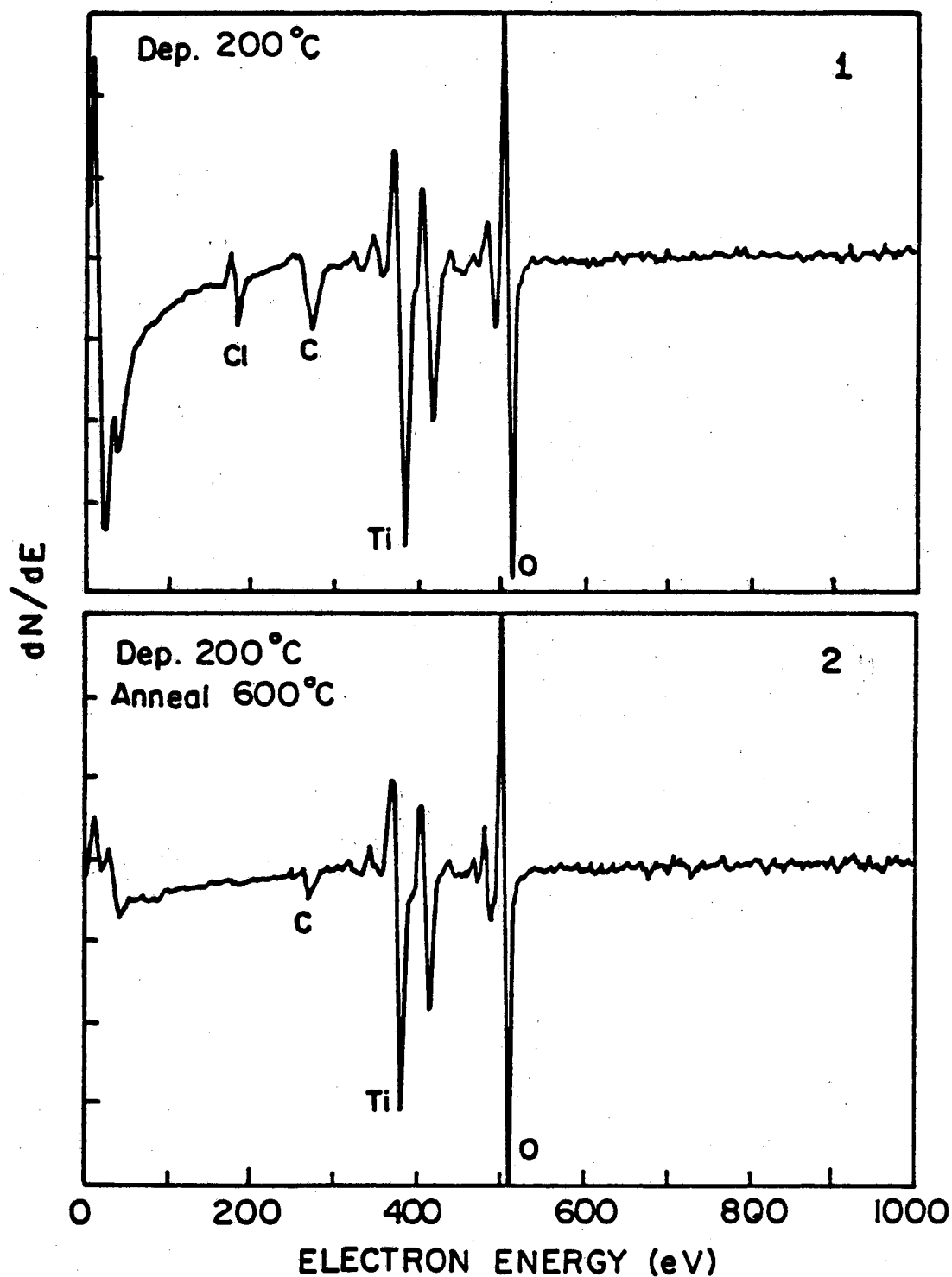
3.2.1 Auger Electron Spectroscopy

Figure 13-1 shows an Auger electron spectrum for a titanium dioxide film deposited onto a silicon substrate at 200 C. The spectrum shows peaks for Cl, C, Ti, and O at electron energies of 181, 271, 380, and 510 eV respectively (83). The carbon is a contaminant picked up from atmospheric exposure after the deposition; the chlorine is incorporated during the deposition. A section of that sample was annealed in a furnace at 400 C for 20 minutes with an oxygen flow of 100 cc/min. The Auger spectrum after the heat treatment (Figure 13-2) shows a large size reduction for the carbon peak and the chlorine peak. The carbon was probably oxidized to carbon monoxide and dioxide while the chlorine, apparently being only weakly bound, was thermally driven off. Another film deposited under the same conditions described above was examined, and the results are given in Figure 14-1. As before, the chlorine peak was present in the as deposited film. However, after annealing a section of the film at a higher temperature, 600 C rather than 400 C, in oxygen for 30 minutes, the chlorine peak is completely removed from the Auger spectrum, Figure 14-2.



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Fig. 13. AES spectra for titanium dioxide plasma deposited at 200 C on silicon: 1. as-deposited, 2. after annealed at 400 C in oxygen for 20 min.



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Fig. 14. AES spectra for titanium dioxide plasma deposited at 200 C on silicon: 1. as-deposited, 2. after annealed at 600 C in oxygen for 30 min.

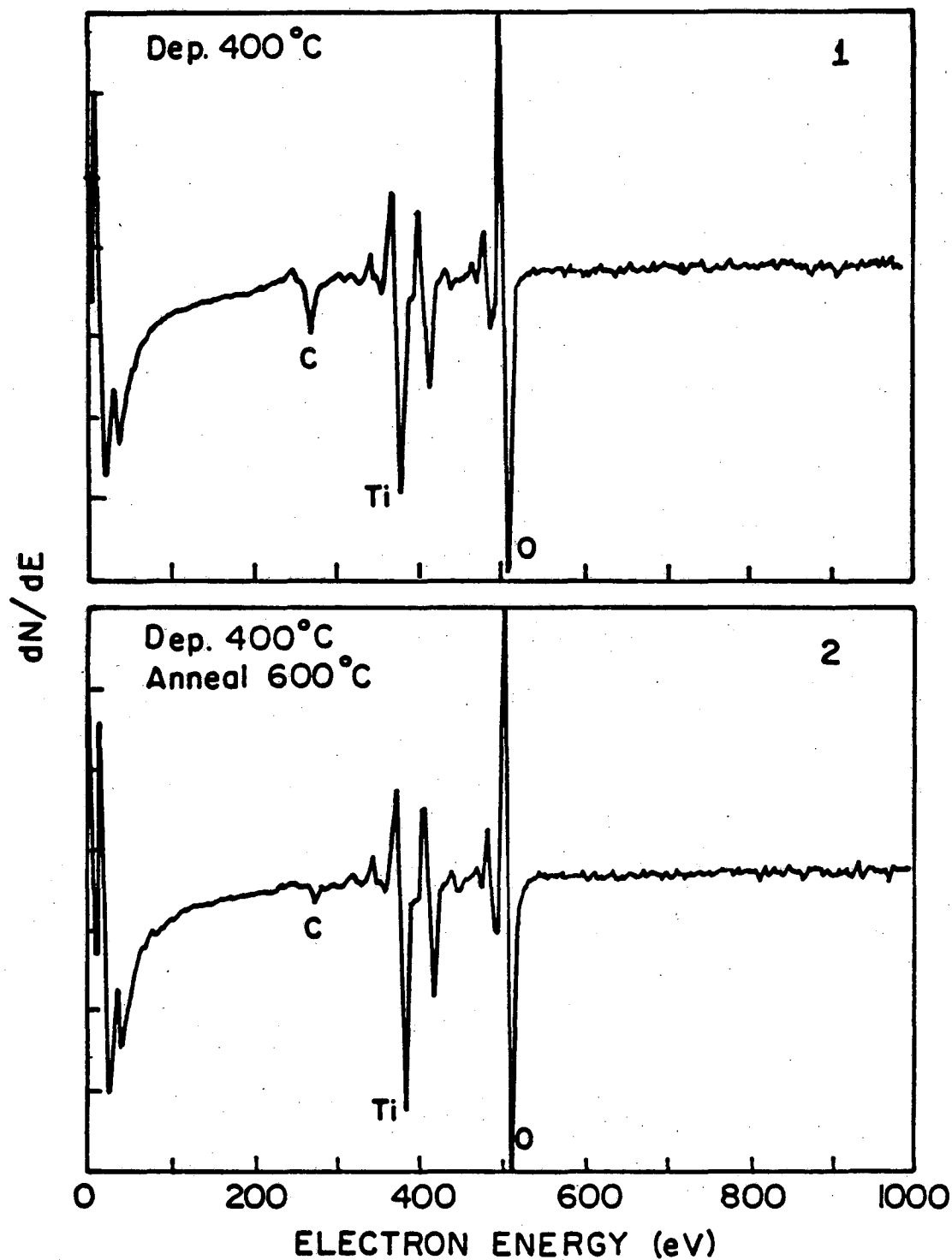
The amount of carbon is also reduced.

When the titanium dioxide films were deposited at 400 C, with the other deposition parameters held constant, the chlorine peak is absent from the Auger spectrum as shown in Figure 15-1. Annealing the film in oxygen for 30 minutes at 600 C left the Auger spectrum of the film unchanged (Figure 15-2) except for a decrease in the amount of carbon.

Atomic concentrations of titanium, oxygen, and chlorine were also calculated using the AES data. The highest concentrations of chlorine were approximately 2 to 3 atomic per cent. On the basis of the chlorine concentrations, the films deposited at 200 C, and then annealed at 600 C were equivalent to the films deposited at 400 C and higher. No chlorine was detectable by AES in films deposited at high temperatures (400 C and higher) or in any film that had been annealed at 600 C.

The peak to peak ratios of oxygen to titanium for the AES measurements are summarized in Table 3. The ratios range from 1.23 up to 1.47 and generally, the high temperature oxygen anneal causes an increase in the ratio. Based on the structural properties (see Section 3.3), the films deposited at 200 C are amorphous and become at least partially crystalline after the 600 C anneal. The 400 C deposition is a mixture of anatase and rutile.

Chung et al. (84) used AES to examine the (100) and (110) surfaces of rutile and found oxygen to titanium ratios ranging from 1.3 to 1.7. Armstrong and Quinn (85) found the



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Fig. 15. AES spectra for titanium dioxide plasma deposited at 400 C on silicon: 1. as-deposited, 2. after annealed at 600 C in oxygen for 30 min.

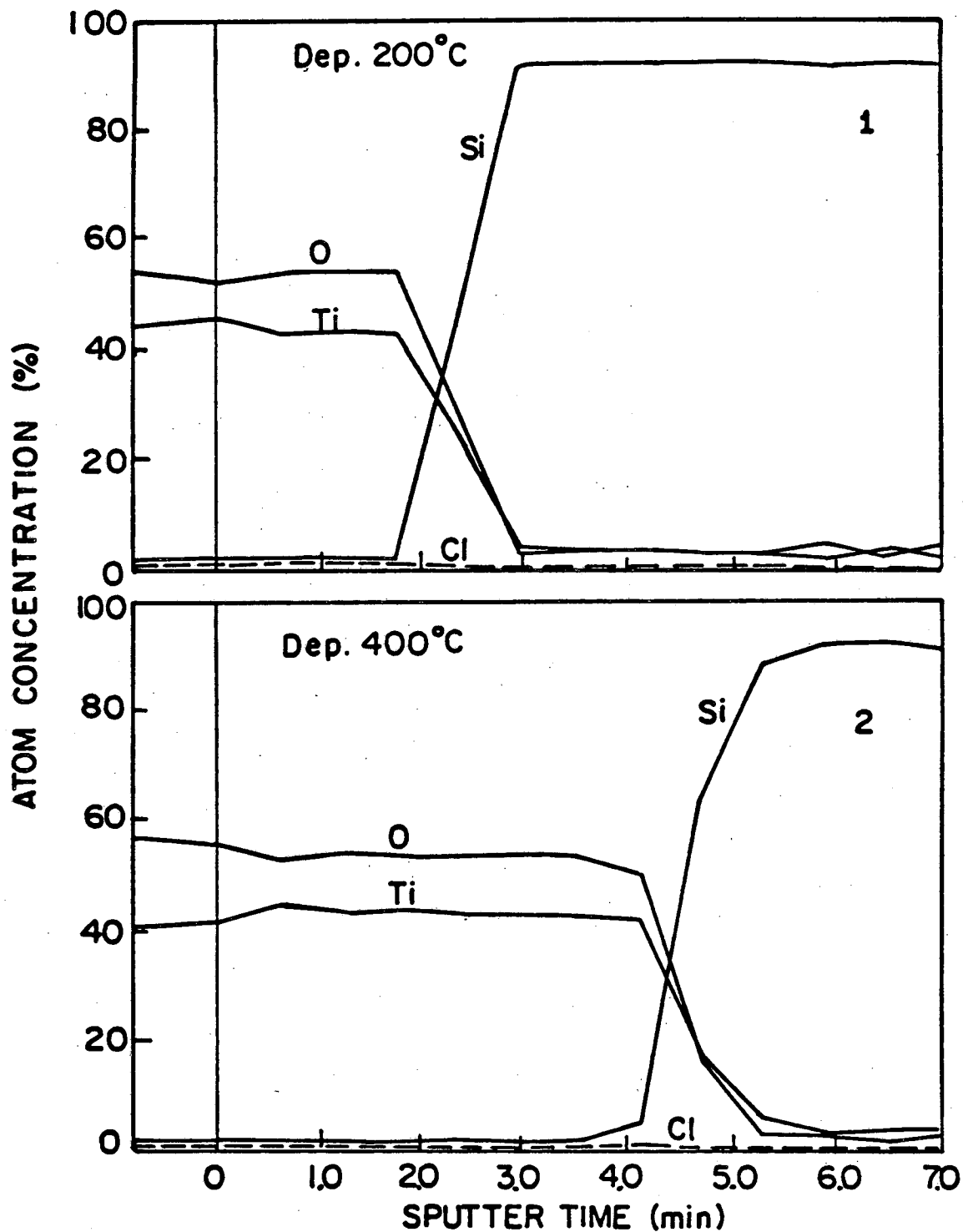
Table 3. Surface Composition From Auger Electron Spectroscopy

Deposition Temp. (C)	Anneal Temp. (C)	Oxygen to Titanium Ratio
200	---	1.33
200	400	1.26
200	---	1.23
400	600	1.47
400	---	1.24
400	---	1.28
400	600	1.30

ratio to be about 1.65 for anodically grown titanium oxides. Both investigators reported that high energy electron and ion beams selectively remove oxygen from the titanium dioxide surface. Chung et al. further state that electron beams of 1.6 kV, usually used for AES, tend to disorder the surface. In the present study, the electron beam energy was 2 kV. This could partially explain the lower oxygen to titanium ratios measured for this study. However, the fact that the ratio is not constant for all the depositions and heat treatments is proof that the electron beam damage does not completely mask the differences in film composition. It is probable that the chlorine is also preferentially removed and thus is present in the film at a higher concentration than was measured.

According to Chung et al. (84), argon ion bombardment of the titanium dioxide surface gave the lowest oxygen to titanium ratio while oxygen ion bombardment did not change the surface. During the plasma enhanced deposition of the titanium dioxide, the surface is continuously bombarded by a mixture of ions -- oxygen ions, chlorine ions, titanium chloride ions and also electrons. This ion bombardment probably plays a large and very complicated role in determining the exact film composition.

Figure 16 shows the concentration profiles of films deposited at 200 C and 400 C. The atomic concentrations of oxygen, titanium, and silicon were recorded at intervals during the sputtering process. In both cases, except for



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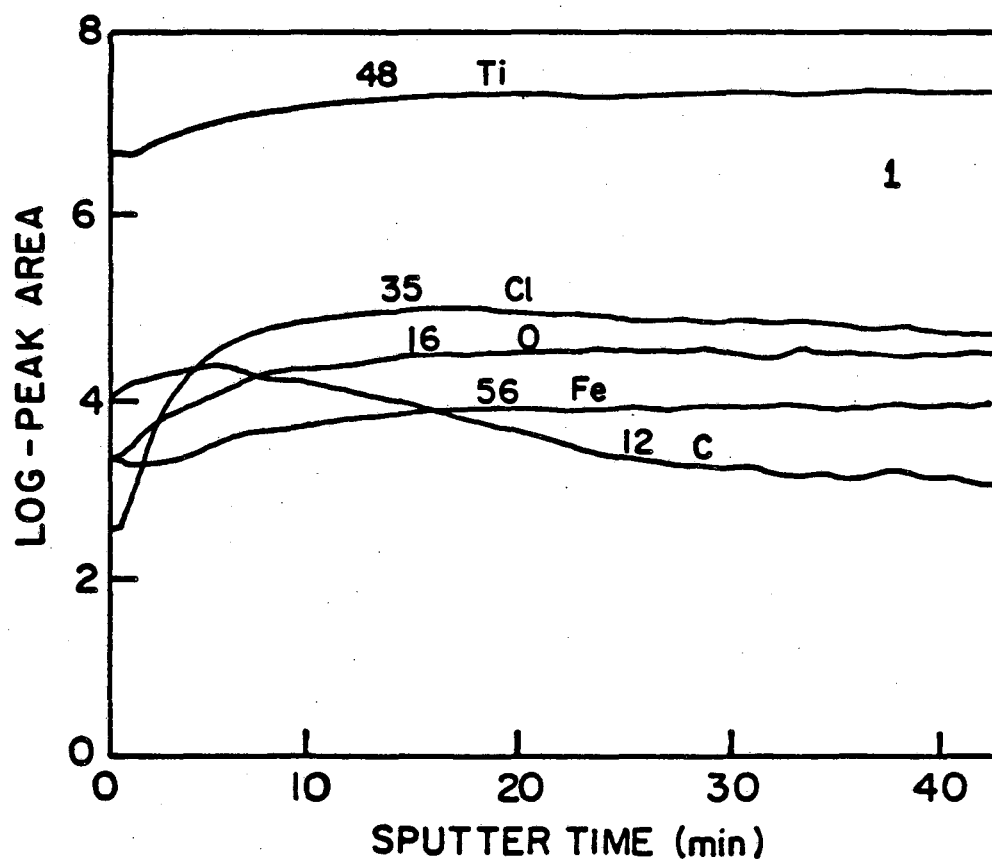
Fig. 16. AES composition profile titanium dioxide deposited on silicon: 1. deposited at 200 C, 2. deposited at 400 C.

minor variations near the surface, the oxygen and titanium concentrations are constant throughout the films. It is also interesting that the films are similar in thickness (135 nm for the 200 C case and 150 nm for the 400 C case) yet the sputtering time required to reach the silicon substrate for the 400 C deposit is more than twice that for the 200 C deposit. Apparently, the 200 C deposit, being amorphous, is much easier to sputter than the polycrystalline 400 C deposit.

3.2.2 Secondary Ion Mass Spectroscopy Profiles

SIMS measurements were performed on a titanium dioxide film deposited onto a titanium substrate at 200 C. The profile data, shown in Figure 17, are analogous to the AES results. Again, with the exception of the near surface region, the titanium concentrations are constant throughout the film. Carbon and chlorine are also shown to be present. Unlike the AES results, the SIMS data indicate the presence of an additional element with a mass to charge ratio of 56. The element is probably iron. It is either incorporated from the walls of the reactor during the deposition or from the substrate. The substrate is a good possibility since it was only 99.7% titanium.

A SIMS profile was also recorded for a titanium dioxide film thermally grown by oxidizing a titanium substrate in oxygen at 700 C for 30 minutes followed by a 30 minute reduction at 600 C in a mixture of 10% hydrogen and 90%



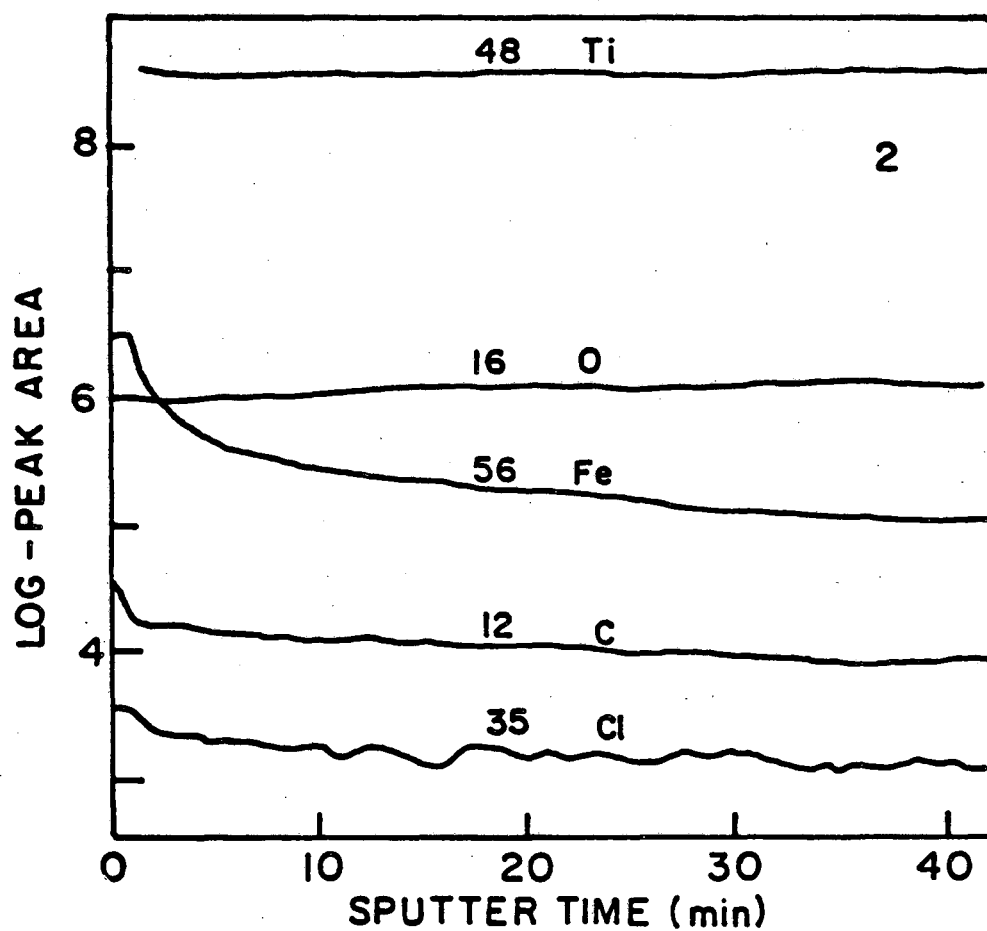
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Fig. 17. SIMS composition profile: titanium dioxide deposited onto titanium at 200 C.

helium. The SIMS profile, shown in Figure 18, is very similar to that for the deposited film. Again, iron, apparently arising from the substrate, is present.

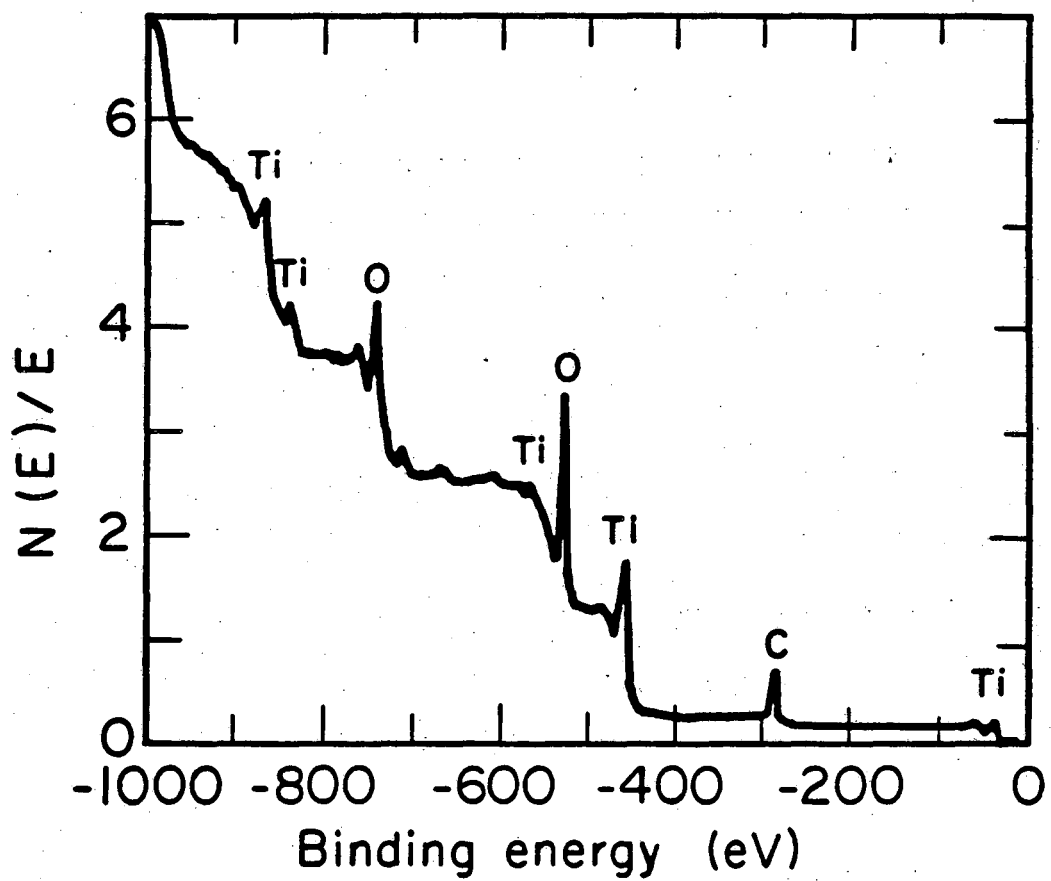
3.2.3 Electron Spectroscopy for Chemical Analysis

ESCA measurements were made for titanium dioxide films deposited onto titanium substrates at 200, 400, and 600 C and the thermally grown film described above. Figure 19 shows a typical ESCA spectrum for a film deposited at 600 C. The ESCA results support the data given by the other techniques. According to the ESCA results, the amount of iron present in the films was very small. And like the AES results, trace levels of chlorine were detected in the films deposited at 200 and 400 C, but none could be found in the films deposited at 600 C.



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Fig. 18. SIMS composition profile: titanium dioxide thermally grown on titanium at 700 C in oxygen.



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Fig. 19. ESCA spectrum for titanium dioxide deposited onto titanium at 600.

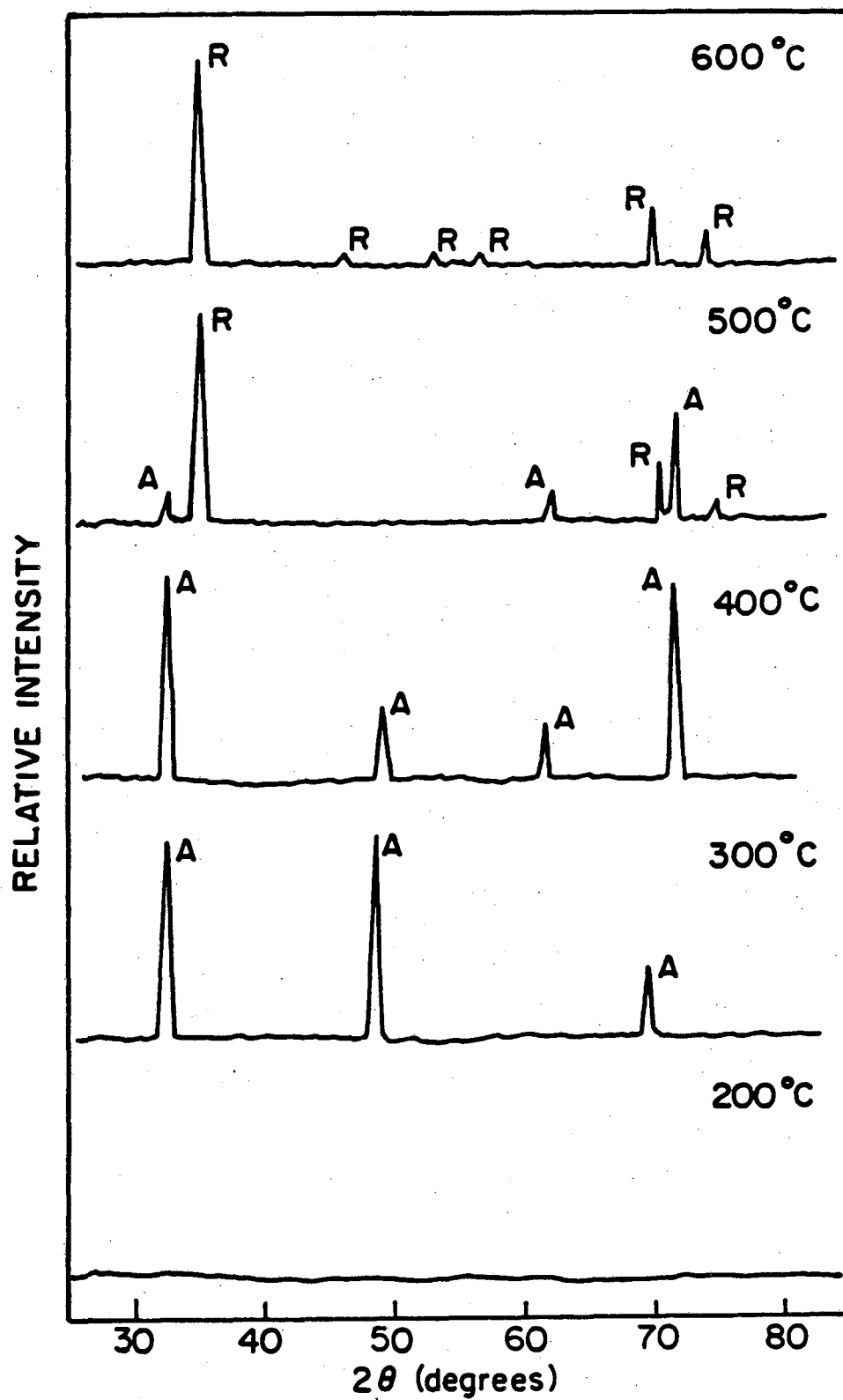
3.3 Film Structure

3.3.1 Glass Substrates

Thin films of titanium dioxide were deposited onto glass substrates for x-ray diffraction analysis. The x-ray diffractometer described in Section 2 provided diffraction patterns using Fe K alpha radiation. In all cases the peaks occurring in the diffraction patterns can be assigned to either anatase or rutile.

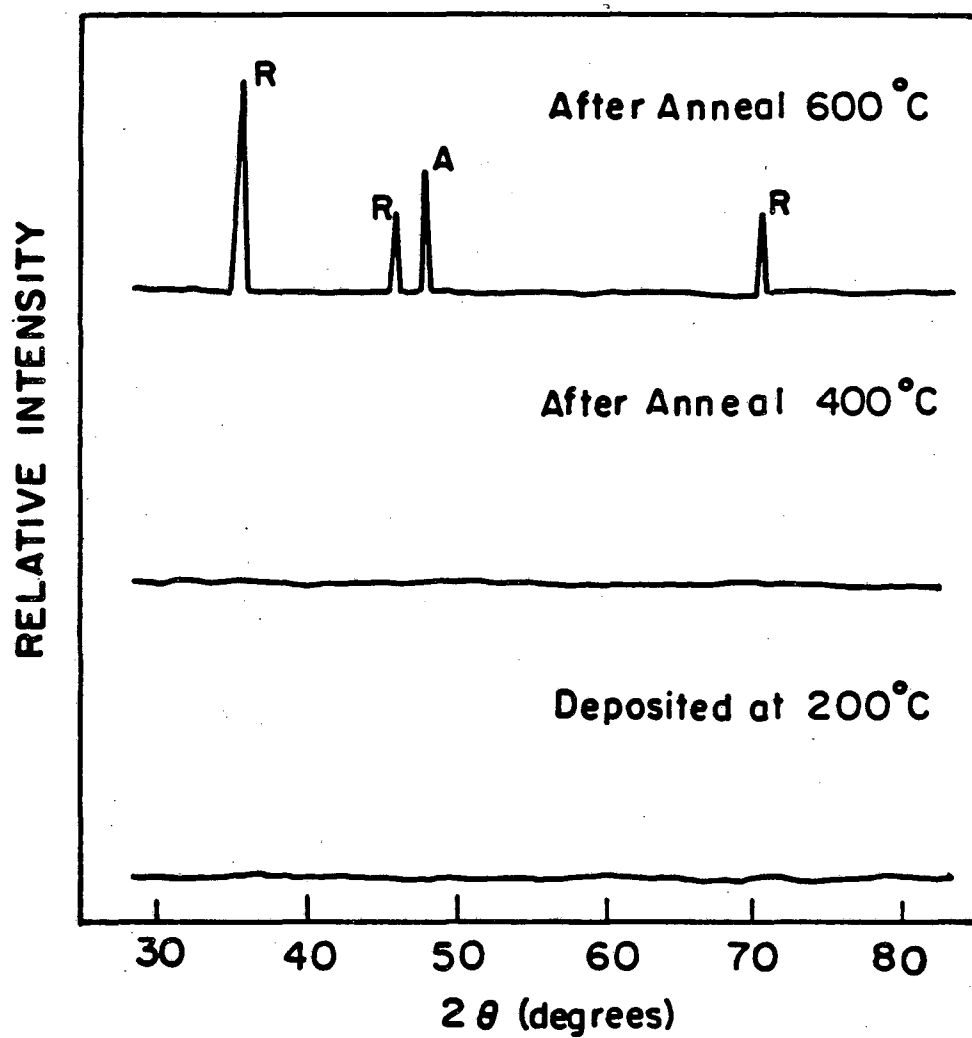
Figure 20 shows x-ray diffraction results for five films deposited at 150 mtorr and ten watts rf power at different temperatures. The film deposited at 200 C gives no diffraction peaks, thus indicating an amorphous state or the presence of very small crystallites. For the depositions at 300 and 400 C, all of the peaks can be attributed to the anatase phase; the observed peak intensities are greater for the 400 C film. The diffraction pattern for the 500 C deposition contains peaks for both the anatase and rutile modifications, whereas, in the 600 C deposition only the rutile phase occurs.

Several films were also annealed in oxygen at temperatures higher than their deposition temperatures in order to determine possible changes in the x-ray diffraction properties. Figure 21 contains the results for three films deposited at 200 C. As expected, no diffraction peaks are observed for the film without subsequent heat treatment. Annealing one of the films at 400 C in oxygen for 20 minutes



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Fig. 20. X-ray diffraction spectra: titanium dioxide deposited onto glass (Fe k alpha radiation).



XBL 828-6285

Fig. 21. X-ray diffraction spectra: titanium dioxide deposited at 200 C then annealed (Fe k alpha radiation).

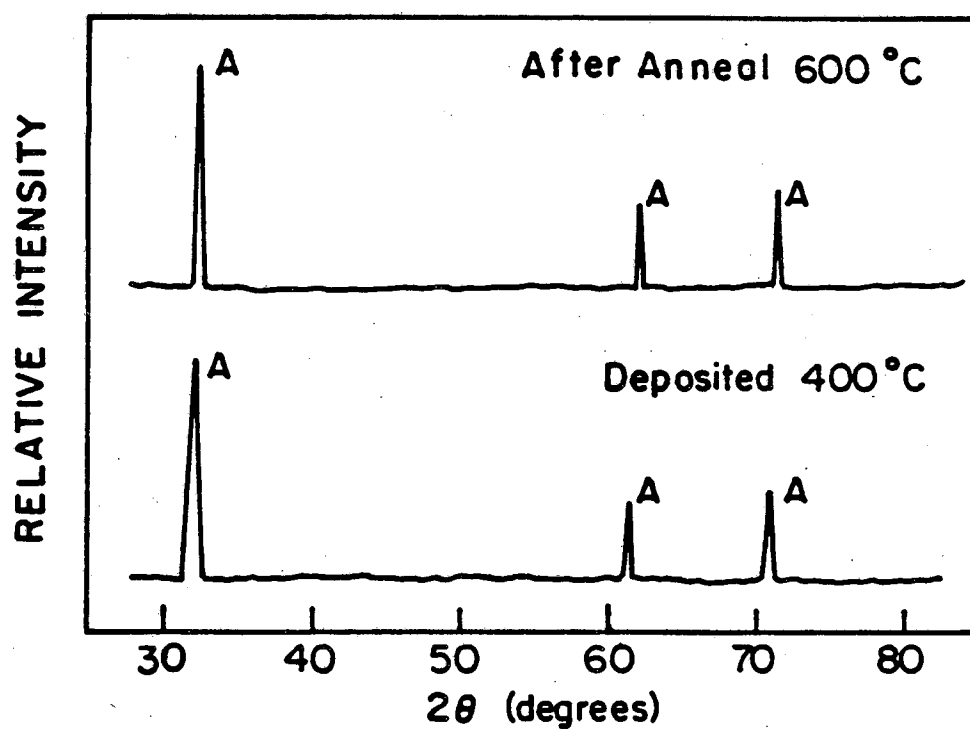
also gave no indication of crystal structure. After annealing the third film at 600 C in oxygen for 30 minutes, the film gives a diffraction pattern indicating rutile; however, one anatase peak also occurs.

Two films were also deposited at 400 C. After annealing one of the films at 600 C in oxygen for 30 minutes, the diffraction pattern is essentially unchanged as is shown in Figure 22.

In x-ray diffraction patterns, preferred orientations are indicated if the relative intensities of several reflections deviate from the ratios found in randomly oriented powder samples (131). Tables 4 and 5 contain the relative intensity data for randomly oriented anatase and rutile from the JCPDS File (132) along with relative intensity data for deposited anatase films (300 and 400 C) and a rutile film (600 C). In all three cases, the deposited films differ from the random orientation cases.

3.3.2 Sodium Chloride Substrates

In order to obtain samples for transmission electron microscopy, several films were deposited onto sodium chloride substrates. These substrates were chosen because the sodium chloride can be easily removed by immersion in water, thereby releasing the film for transmission electron microscopy. The main purpose for the TEM studies was to observe crystallite sizes and, particularly, to determine if the low temperature depositions (200 C) were amorphous or



XBL828-6287

Fig. 22. X-ray diffraction spectra: titanium dioxide deposited at 400 C then annealed (Fe k alpha radiation).

Table 4. Preferred Orientation In Plasma Deposited Anatase

d (Å)	Relative Intensity Random Anatase Crystallites (132)	Relative Intensity Plasma Deposited Anatase	
		300 C	400 C
3.52	100	94	100
2.431	10	100	
2.378	20	20	
2.332	10		
1.892	35		22
1.699	20	31	
1.666	20		94

Table 5. Preferred Orientation In Plasma Deposited Rutile

d (Å)	Relative Intensity Random Rutile Crystallites (132)	Relative Intensity Plasma Deposited Rutile 600 C
3.25	100	100
2.487	50	5
2.293	8	
2.188	25	5
2.054	10	4
1.687	60	27
1.624	20	12

possessed very small crystallites.

Transmission electron micrographs and diffraction patterns for films deposited at 300, 400, 600, and 700 C are shown in Figures 23-26. The film deposited at 300 C, Figure 23, has a diffraction pattern that indicates it is amorphous. The micrograph shows the presence of circular structures, approximately 200 nm in diameter, but they are not individual crystallites.

For a deposition temperature of 400 C, the electron diffraction pattern has rings indicating a polycrystalline structure. The d spacing for some of the rings were calculated (see Appendix for details) and used in an attempt to identify the phase present. The information is summarized in Table 6. Unfortunately, either the d values that could be determined could be attributable to both anatase and rutile, or the d spacings were below the range reported in the " Powder Diffraction File" (132) . The crystallites for the 400 C deposition can easily be seen in Figure 24. Typical crystalite dimensions were in the range of 30 to 50 nm.

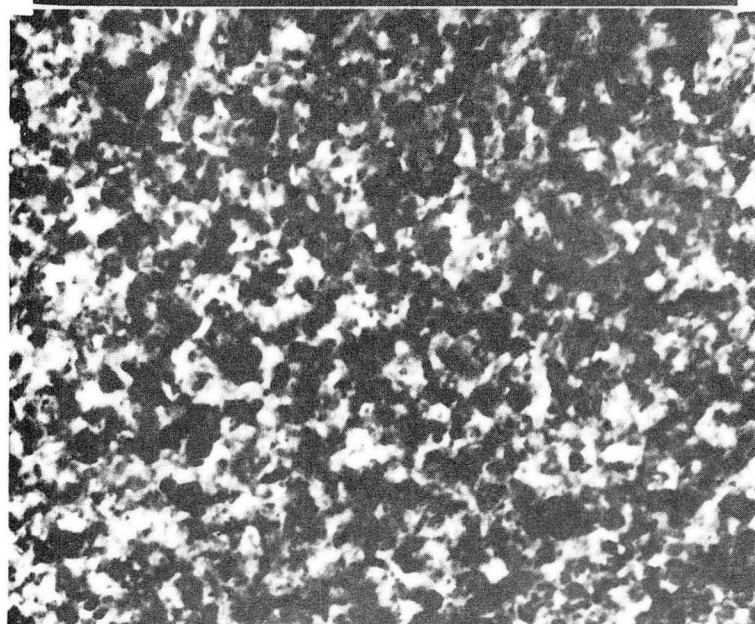
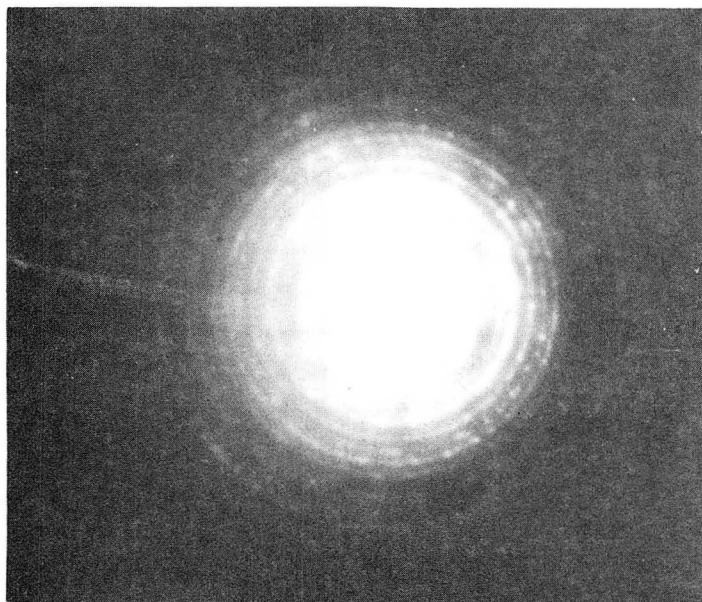
A ring pattern was also observed for films deposited at 600 C, (Figure 25). However, in this case the rings were broken into arcs thus indicating preferred orientations (86). Based on the d spacing calculations, both the anatase phase and the rutile phase are present at this temperature, Table 6. Many of the crystallites have dimensions in the 80 to 100 nm range.

Fig. 23. TED (top) and TEM (bottom): titanium dioxide deposited at 300 C.

Fig. 24. TED (top) and TEM (bottom): titanium dioxide deposited at 400 C.

TiO₂ Film Deposited at 400°C

NaCl Substrate



2500 Å

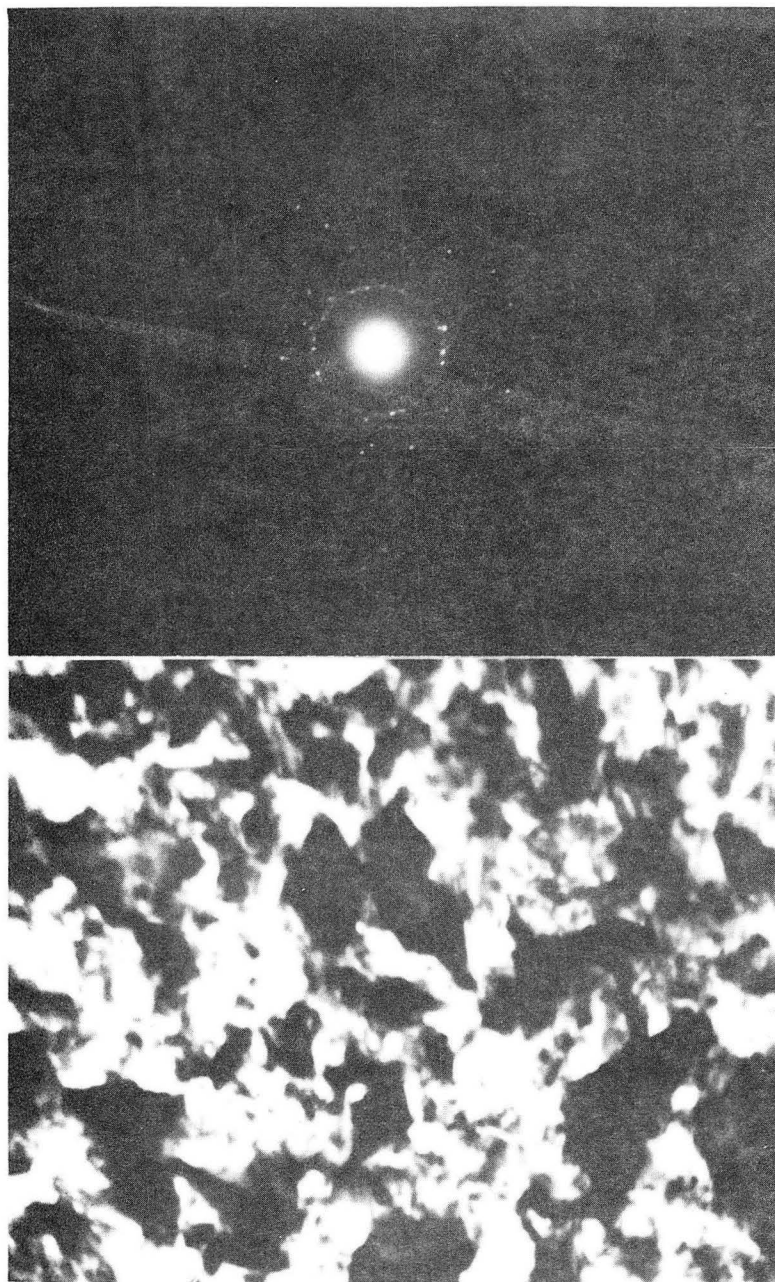
XBB 823-1920

Fig 24

Fig. 25. TED (top) and TEM (bottom): titanium dioxide deposited at 600 C.

Fig. 26. TED (top) and TEM (bottom): titanium dioxide deposited at 700 C.

TiO₂ Film Deposited at 700°C
NaCl Substrate



2500 Å

XBB 823-1918

Fig 26

Table 6. Transmission Electron Diffraction Data

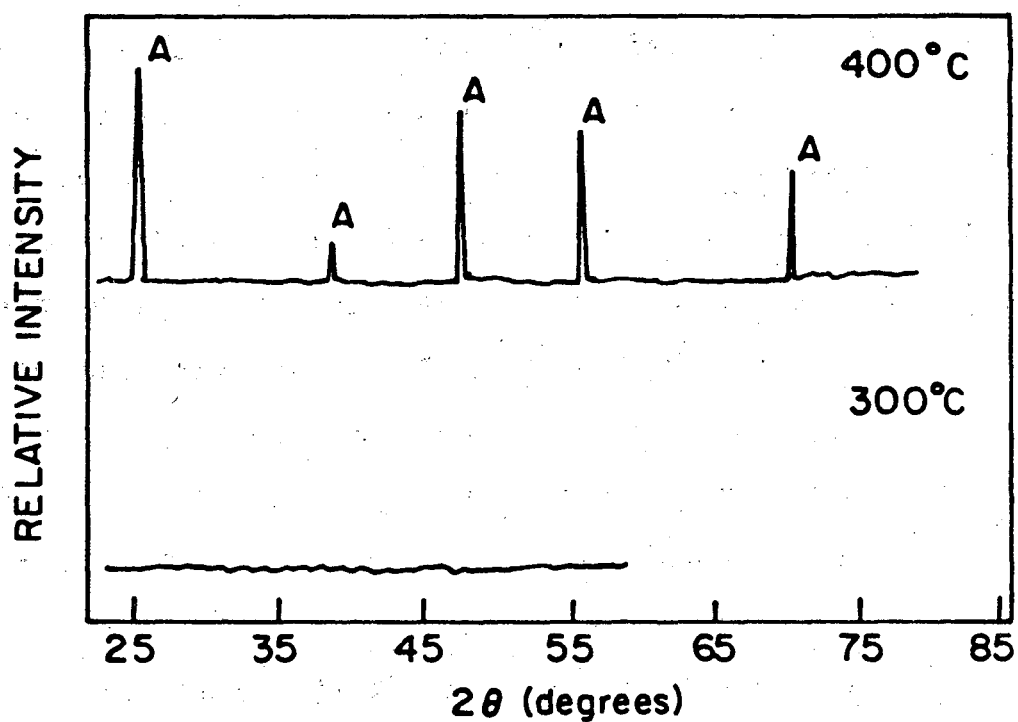
Sodium Chloride Substrates (single crystal)
 Camera constant = 1.707 angstrom-cm

d (A) Calculated From TED Plasma Deposited Films (132)	Anatase d (A) Ref. (132)	Rutile d (A) Ref.
400 C		
1.72	1.70	1.69
1.20	1.25	1.20
0.96		
0.85		
600 C		
3.19		3.25
2.40	2.38	2.29
1.80	1.89	
1.42	1.36	1.42
1.19	1.25	1.20
1.05		
700 C		
1.67	1.67	1.69
1.39	1.36	1.36
1.20	1.25	1.20

The diffraction pattern for the film deposited at 700 C, Figure 26, shows more of a spot pattern. This indicates that the crystallites are more closely aligned than in the previous films (86). Some of the larger crystallites have dimensions of about 250 to 300 nm. Again, the calculated d spacing values could be due to anatase or rutile. The film is probably a mixture of the two phases.

X-ray diffraction measurements were also made on some of the films deposited onto NaCl. The titanium dioxide films deposited onto NaCl cracked and peeled after cooling to room temperature. (This is believed to be the result of the differences in the thermal expansion coefficients: 41 E-6 per degree C for sodium chloride (70), 9.2 E-6 per degree C for titanium dioxide (32).) To get around this problem, a piece of Scotch tape was applied to the titanium dioxide film immediately after it cooled. The sodium chloride was subsequently dissolved away. The tape and titanium dioxide were then placed in the x-ray diffractometer with the titanium dioxide facing up.

Generally, the x-ray diffraction results gave the same information, in terms of identifying the phases, as the electron diffraction. X-ray diffraction results for deposits made at 300 and 400 C are given in Figure 27. The 300 C deposition did not give any diffraction peaks, suggesting an amorphous structure. The film deposited at 400 C apparently contained anatase and no rutile.



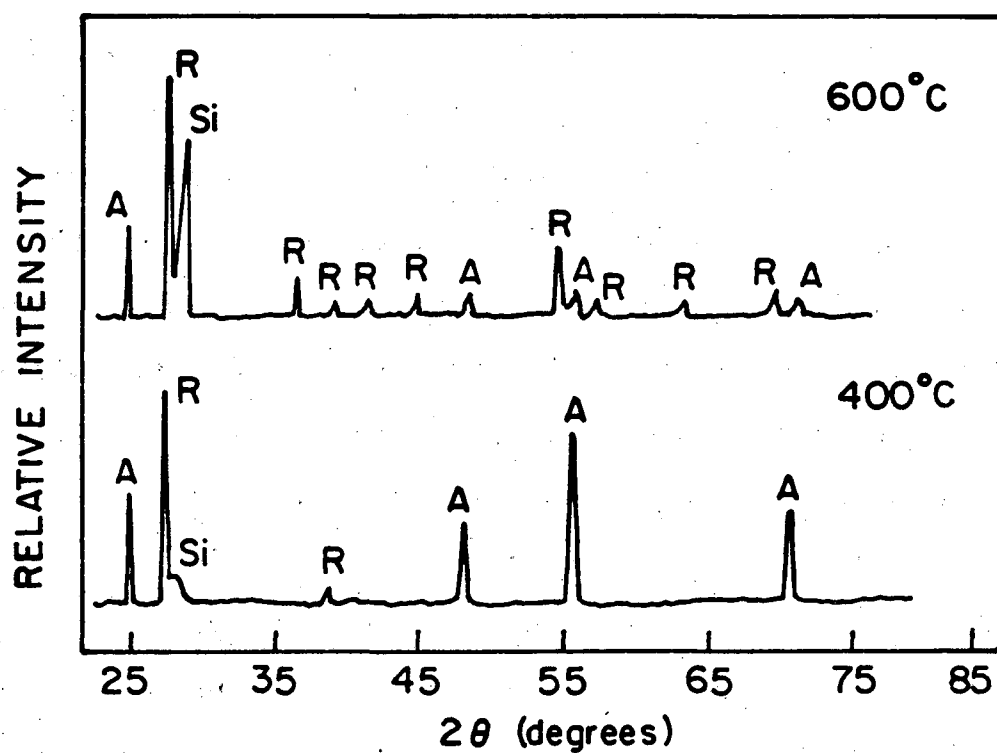
XBL 828-6291

Fig. 27. X-ray diffraction spectra: titanium dioxide deposited onto NaCl (Cu k alpha radiation).

3.3.3 Silicon Substrates

There are two very important differences between the structural properties of the films deposited onto silicon substrates ((111) orientation) and those deposited onto glass substrates. As can be seen in Figure 28, strong anatase and rutile peaks are present in the x-ray diffraction patterns for the 400 C deposition. Such behavior was not observed for the films deposited onto glass until the deposition temperature was raised to 500 C. In addition, the anatase-rutile mixture continues to exist at 600 C while only rutile occurs when glass substrates are used. These observations indicate that silicon substrates probably have some nucleation sites that are more favorable (higher in energy) for rutile formation than does glass at similar temperatures. The fact that there is still a mixture of the two phases on silicon substrates at higher temperatures than for glass suggest that the active site (nucleation site) energies for silicon are initially higher but increase more slowly with temperature than for glass.

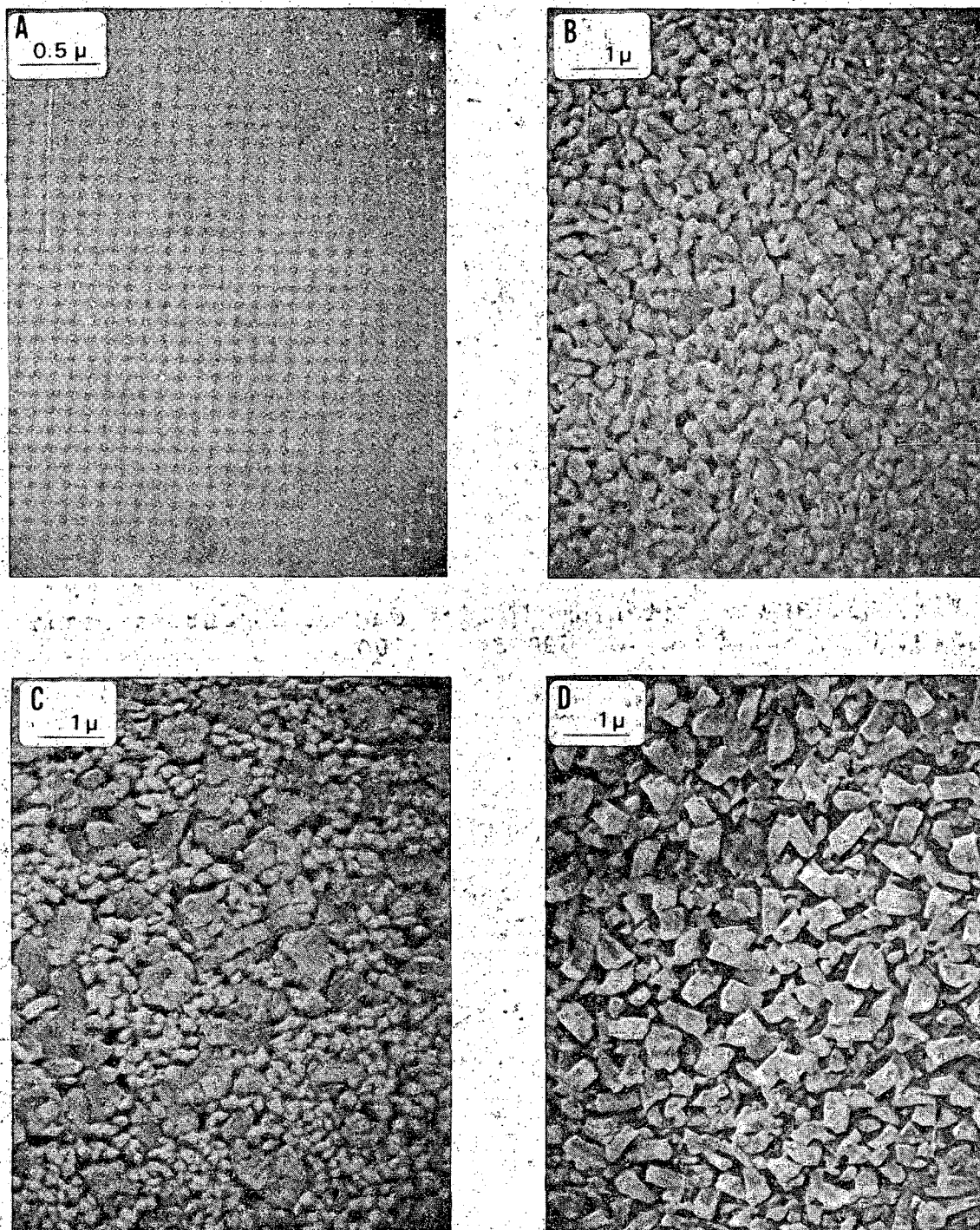
SEM photographs of the four films deposited on silicon are given Figure 29. The film in Figure 29-A was deposited at 200 C. It is smooth, crackfree, and shows no signs of crystal structure. Figure 29-B, for a film deposited at 400 C, shows the presence of crystallites with dimensions of approximately 400 nm. The size distribution appears uniform, whereas, the crystallites in Figure 29-C have a bimodal distribution. The larger crystals (dimensions of



XBL 828-6290

Fig. 28. X-ray diffraction spectra: titanium dioxide deposited onto silicon (Cu k alpha radiation).

Fig. 29. SEM of titanium dioxide deposited onto silicon at:
A. 200 C, B. 400 C, C. 600 C, D. 700 C.



XBB 828-7399

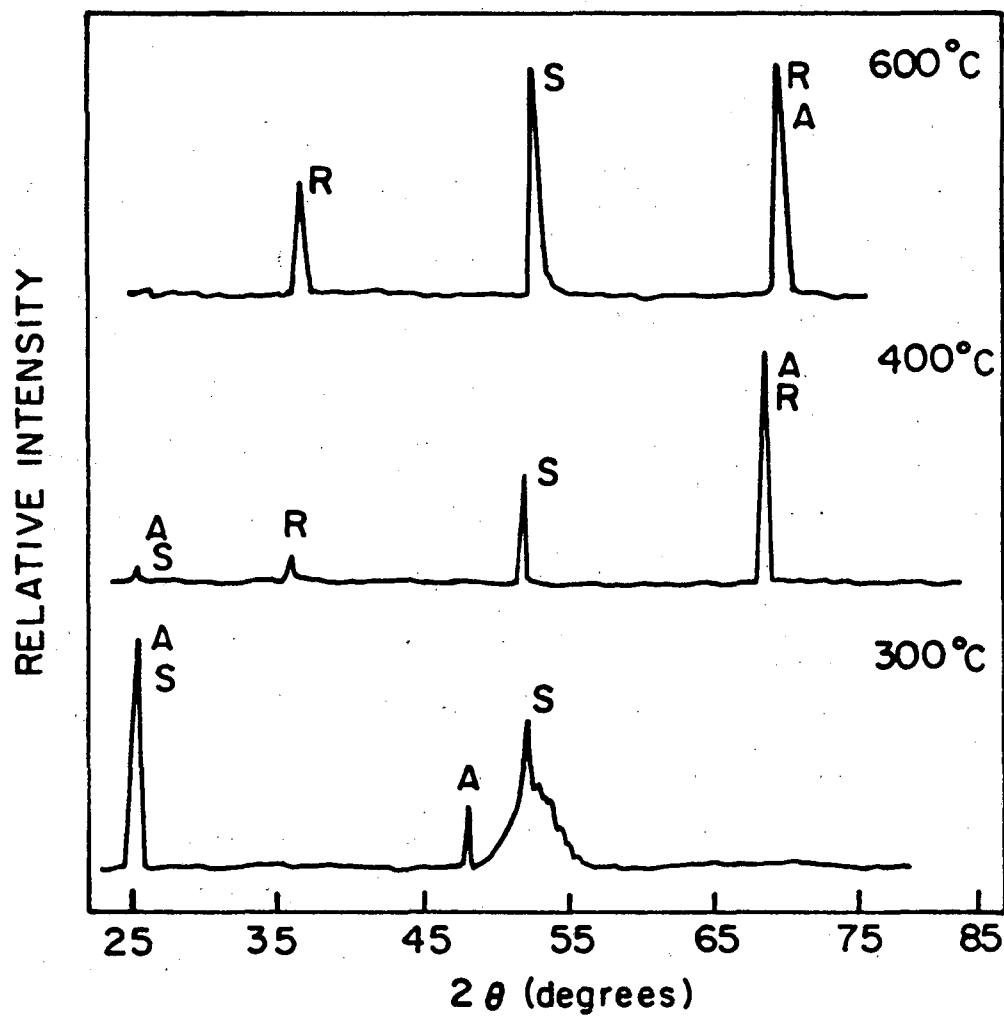
Fig 29

800 nm) are probably anatase and the smaller crystals (dimensions of about 250 nm) are probably rutile. This behavior agrees with the x-ray diffraction results (Figure 28). For the 700 C deposit, Figure 29-D, the crystallite distribution is homogenous and is probably only rutile (dimensions of about 700 nm).

3.3.4 Sapphire Substrates

The structural properties of titanium dioxide films deposited onto single crystal sapphire substrates ((1-102) orientation) were examined. The x-ray diffraction properties are more difficult to interpret than for the other substrates because the films show a higher degree of preferred orientation. The preferred orientation results in fewer titanium dioxide peaks, thus the problem of identifying which phases are present is compounded. In addition, the sapphire substrate has a diffraction peak for $d=3.52$ angstroms (25.3 degrees for Cu k alpha radiation) which overlaps a diffraction peak for anatase.

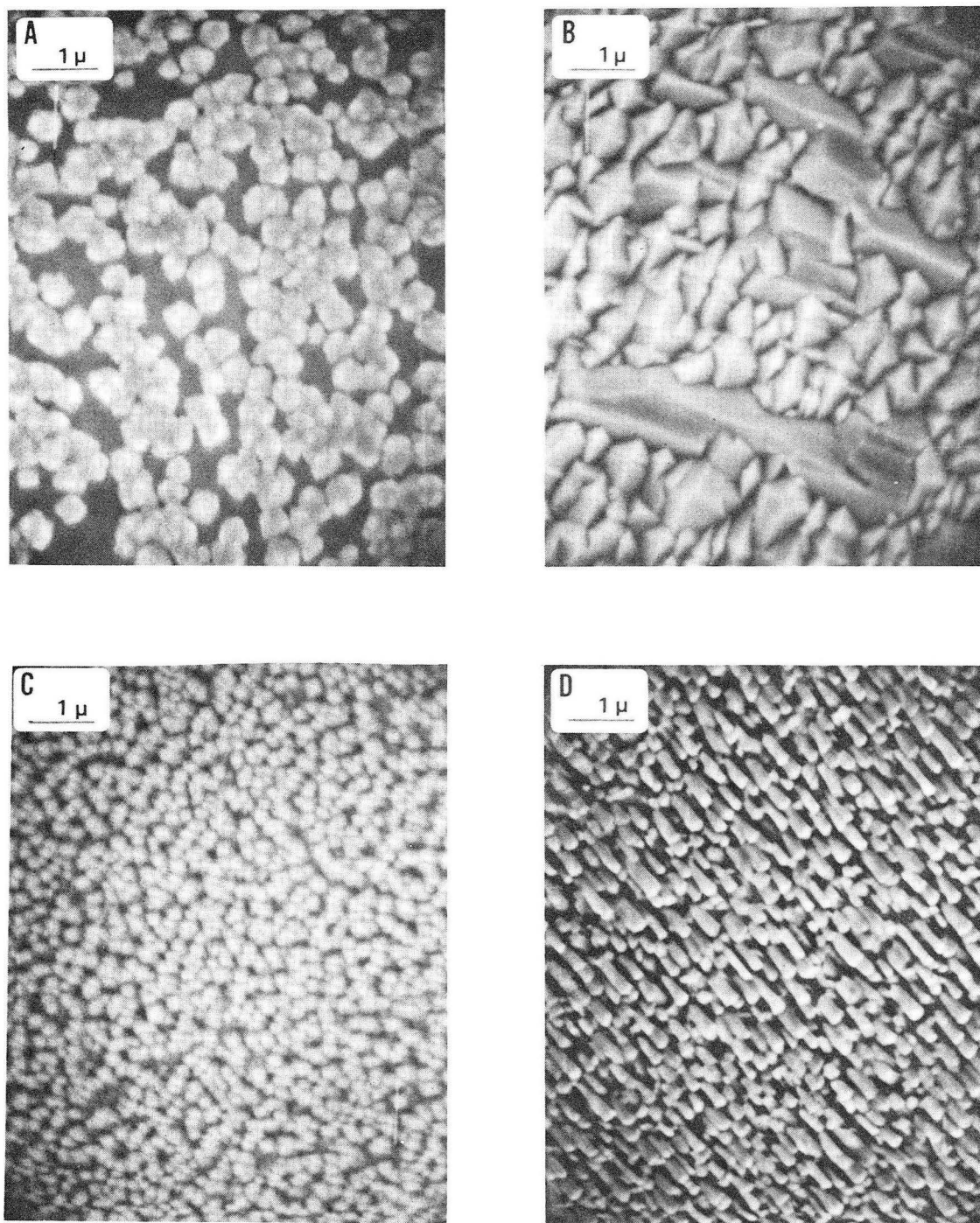
Overall, the x-ray diffraction properties of titanium dioxide deposited on sapphire show the same trends as do the other substrates. Some of the x-ray diffraction properties for films deposited at three different temperatures are given in Figure 30. The film deposited at 300 C contains only anatase crystallites; all of the peaks can be attributed to anatase or to the sapphire substrate. For the films deposited at 400 C and 600 C, one can only say that



XBL 828-6293

Fig. 30. X-ray diffraction spectra: titanium dioxide deposited onto sapphire: temperature series (Cu k alpha radiation).

Fig. 31. SEM of titanium dioxide deposited onto sapphire at:
A. 300 C, B. 400 C, C. 600 C, D. 700 C.



XBB 828-7397

Fig 31

there is some rutile in both and the 600 C case has a much larger amount of rutile. The peak at 70.5 degrees (1.33 angstroms) for the 400 C case and the peak at 69.3 degrees (1.37 angstroms) for the 600 C case can be caused by either anatase or rutile. However, in view of the growth behavior of the phases (Section 1.2.1) it is reasonable to assign the peak at 70.5 degrees (400 C deposit) to anatase and the peak at 69.3 degrees (600 C deposit) to rutile.

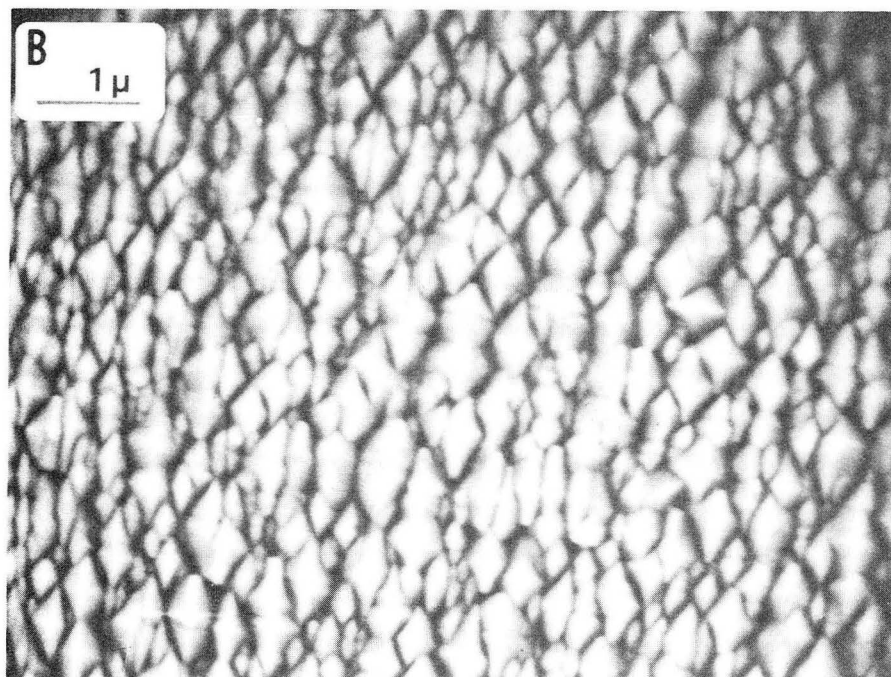
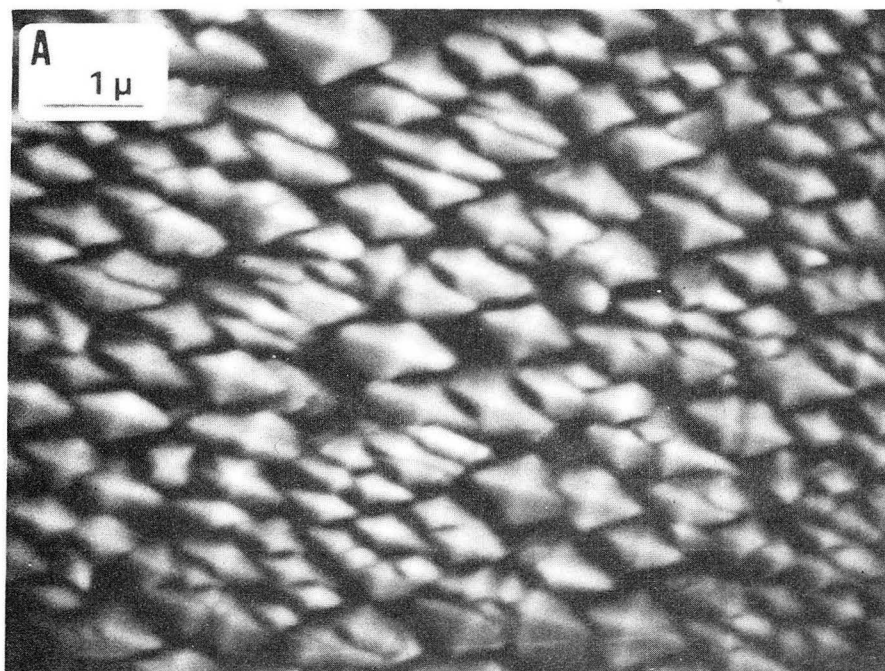
SEM photographs for the three films discussed above are shown in Figure 31. The film deposited at 300 C, Figure 31-A, is probably a mixture of anatase crystallites and amorphous titanium dioxide. As expected, the crystallite size for the film deposited at 400 C, Figure 31-B, is larger than that for the 300 C case. Figure 31-C shows the crystallites for the film deposited at 600 C to be smaller than for the 400 C case. This change in crystallite size with temperature indicates that the dominant crystalline phase is different for the two cases. The primary form present at 400 C is anatase while rutile is the main component for depositions made at 600 C. These observations also support the interpretations given above for the x-ray diffraction results. Figure 31-D shows a film deposited at 700 C. The crystallites for the 700 C film are larger than those for the 600 C deposition and both are believed to be rutile. The preferred orientation for the 700 C deposition can easily be seen in Figure 31-D.

In order to learn more about the structure of films

grown in the temperature range wherein the deposition conditions change from favoring anatase to favoring rutile, two films were deposited at 455 C and 510 C. The SEM photographs of the two films are shown in Figure 32. Apparently, the change from larger crystallites to small crystallites is a gradual process rather than a sharp transition. The larger crystallites at 400 and 455 C are anatase, and they decrease in size as the deposition temperature is raised. Also, at higher deposition temperatures (510 and 600 C), rutile crystallites begin to appear. Though they are initially small, they grow to larger sizes as the deposition temperature is raised.

A qualitative explanation of the growth behavior observed here can be derived from thin film nucleation and growth theories (93,131,133). It is generally accepted that thin films begin to form on surfaces at nucleation sites (93,131,133). The energy of the nucleation sites is a function of temperature, and different types of sites may have different energies. The density of sites is inversely proportional to the site energy (133). Thermodynamically, the rutile form of titanium dioxide is the most stable form. The fact that it does not begin to form except at higher temperatures implies that it has a higher activation energy for formation than does anatase. During the early stages of film growth, the nucleation sites serve the same functions as the active sites used in describing heterogeneous reactions (134); they reduce the activation energy for the

Fig. 32. SEM of titanium dioxide deposited onto sapphire at:
A. 455 C, B. 510 C



XBB 828-7394

Fig 32

reaction. Thus the growth of rutile crystallites requires very high energy nucleation sites (i.e. high temperature).

At deposition temperatures around 400 C, the energies of the nucleation sites are insufficient to allow rutile crystallites to form. However, anatase can be nucleated and can easily grow by coalescence into the large crystallites shown in the SEM photographs. Higher temperatures increase the site energies, but the most energetic sites begin to form rutile crystallites. The surface becomes covered with a mixture of both crystalline phases. This leads to a reduction in average crystallite size because coalescence of crystallites from different phases is probably more difficult (93). The anatase crystallites are larger but can not "absorb" the rutile crystallites because of the higher thermodynamic stability of the rutile. The rutile crystallites are unable to "absorb" the anatase crystallites because the anatase crystallites are too large. (Note: the term "absorb" is used to denote which phase and orientation results after the coalescence). At 600 C either all the nucleated crystallites are rutile or the anatase crystallites are absorbed by the rutile. The result is the same for both possibilities; only the rutile phase occurs at 600 C and higher.

3.3.4.1 RF Power

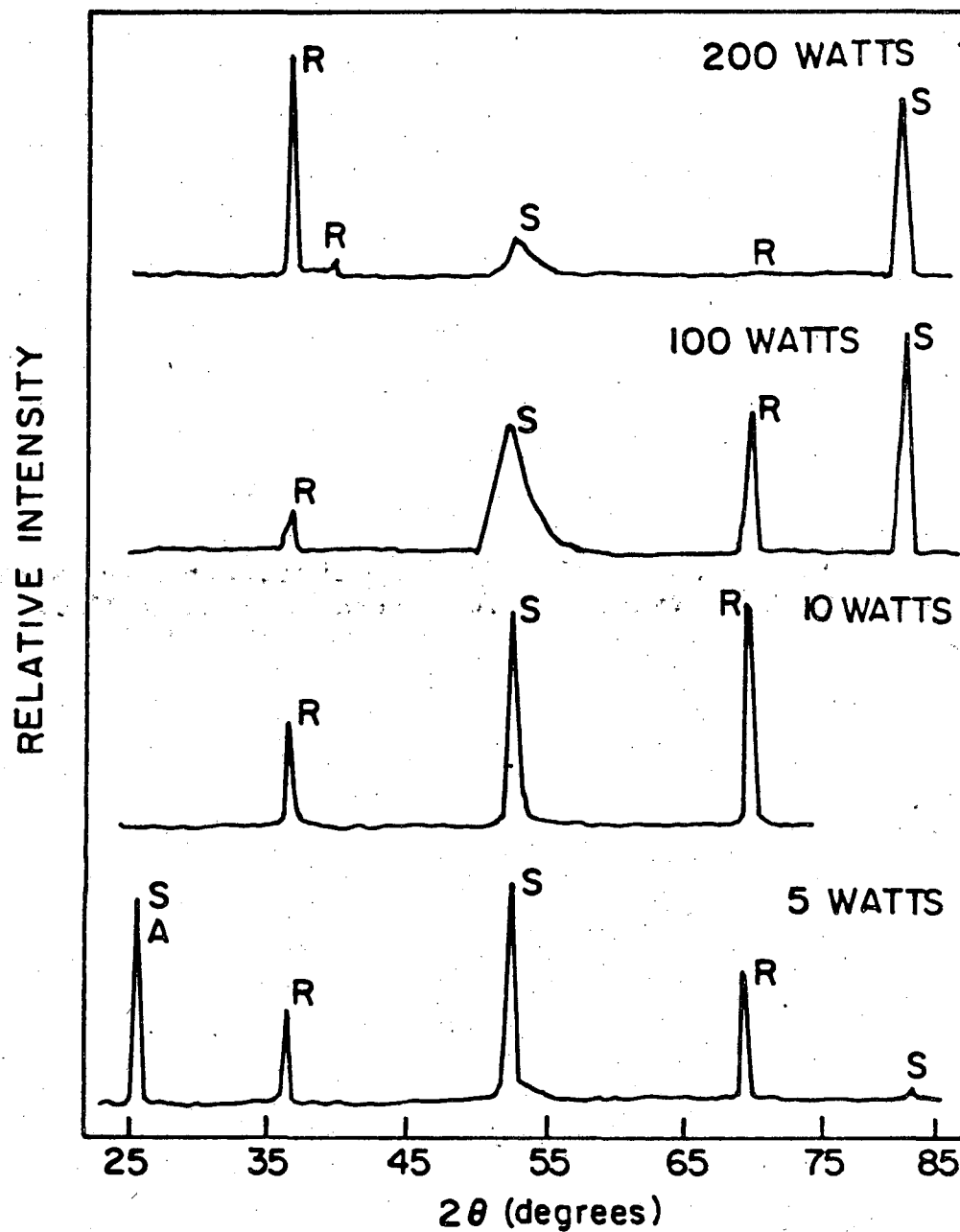
The applied radio frequency power has a large effect on the structural properties of the plasma deposited films.

Figure 33 shows some of the x-ray diffraction properties for four titanium dioxide films deposited onto sapphire substrates at 600 C and rf powers of 5, 10, 100, and 200 watts (0.06, 0.12, 1.2, and 2.4 watts per square centimeter). The diffraction peaks at 25.5, 52.5, and 82.5 degrees are caused by the sapphire substrate. The remaining peaks at 36.4, 39.3, and 70.5 degrees are believed to be due to rutile. The most significant effect of the rf power is the change in actual peak intensity in counts per second. The intensities for all of the titanium dioxide peaks decreased as the rf power input was increased. Similar observations have been reported by Wroge (70) for PED iron and iron oxides. He attributed the reduction in crystallinity to radiation damage caused by ion bombardment. This is a reasonable explanation for the PED titanium oxides since the higher rf power levels correspond to power densities often used for sputtering systems (65).

Differences in the structural properties can easily be seen in the SEM photographs of films deposited at 5, 100, and 200 watts, Figure 34. The film in Figure 34-A was deposited at 5 watts and has crystallites with dimensions of about 300 nm. By comparison, the films deposited at 100 and 200 watts do not have distinct crystalline features as shown in Figures 34-B and C.

3.3.4.2 Efforts to Enhance Crystallite Size

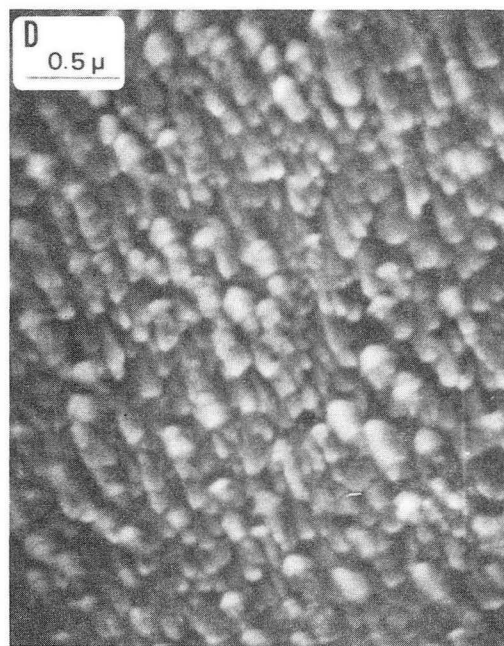
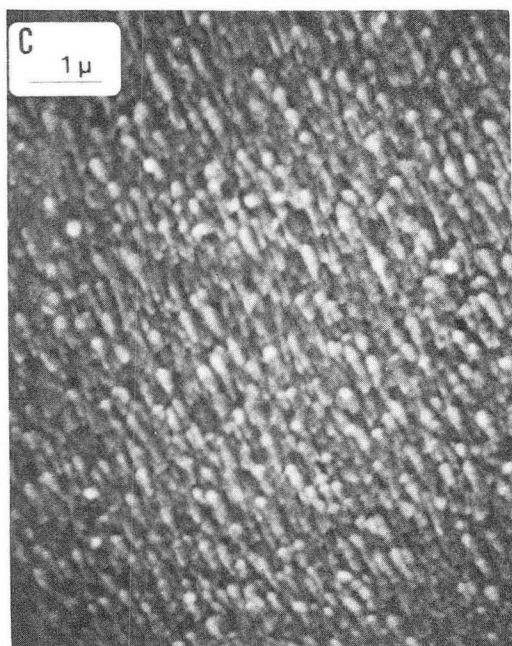
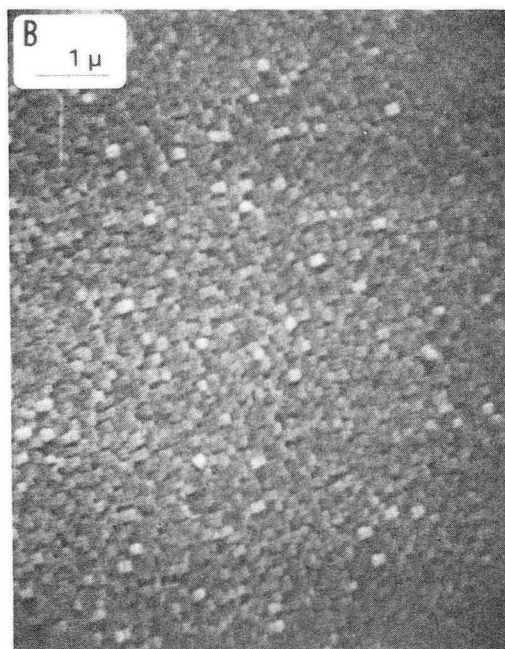
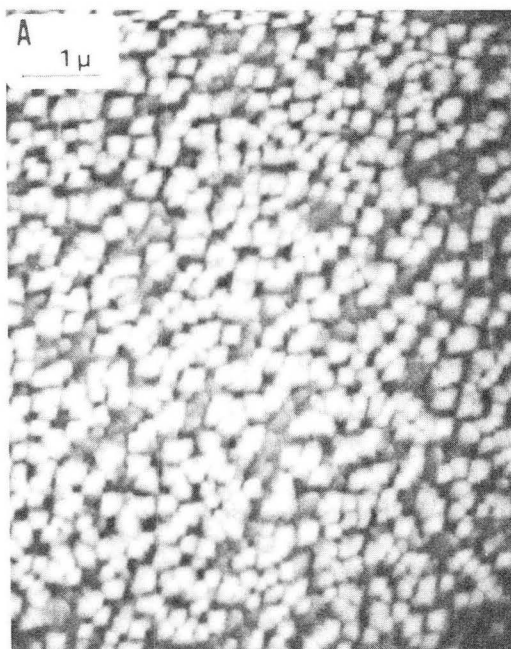
The largest crystallites observed were for depositions



XBL 828-6292

Fig. 33. X-ray diffraction spectra: titanium dioxide deposited onto sapphire: rf power series (Cu k alpha rad.).

Fig. 34. SEM of titanium dioxide deposited onto sapphire: rf power series: A. 5 watts, B. 100 watts, C. and D. 200 watts.



XBB 828-7398

Fig 34

made at about 400 C. In view of this fact, a series of depositions was carried out with the intention of finding the maximum crystallite dimensions possible and thus the best deposition conditions for this purpose. The best possible result would be to obtain single crystal films. Heteroepitaxial deposition of titanium dioxide for the temperature range used in this study would be a very significant accomplishment (to the author's knowledge, the lowest temperature reported for heteroepitaxial deposition of titanium dioxide is 827 C (88)). In addition, the films deposited at 400 C are anatase, and there have been no reports of depositing single crystal anatase films. This may be due to the fact that, at the temperatures required for epitaxial film growth by CVD, the anatase modification is not thermodynamically favored.

The series involved changing the gas flows to modify the deposition rate and changing the rf power levels for deposition and for the oxygen plasma descum. Table 12 (Appendix) summarizes the experimental conditions. Most of the trials produced little, if any, improvement in the grain size. However, there were significant improvements in grain size for two sets of conditions. The gas flow rates and rf powers were the same for both cases: 40 micromoles of titanium tetrachloride per minute, 45 micromoles of oxygen per minute, and 5 watts. Also, for the first case, the gas flow was not throttled to increase the pressure. Instead, helium was bled into the system to bring the pressure up to

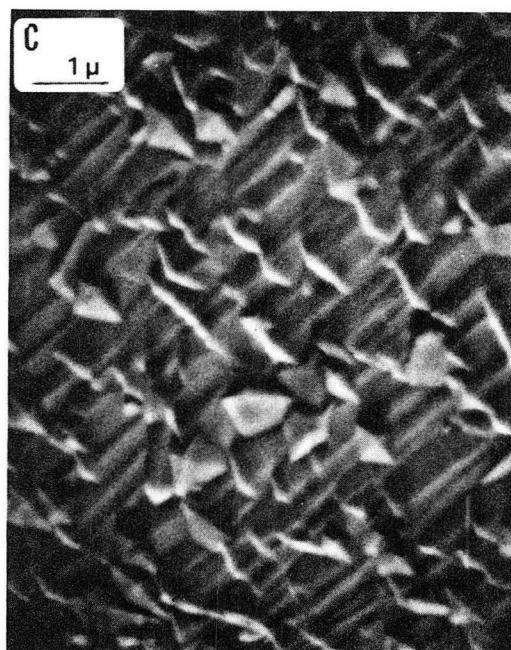
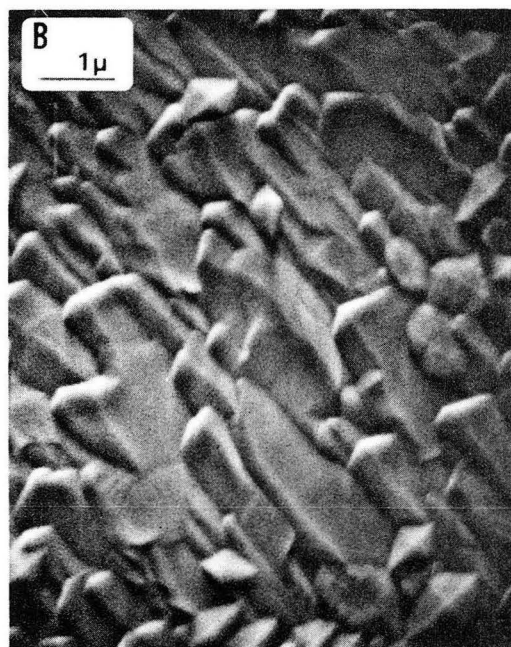
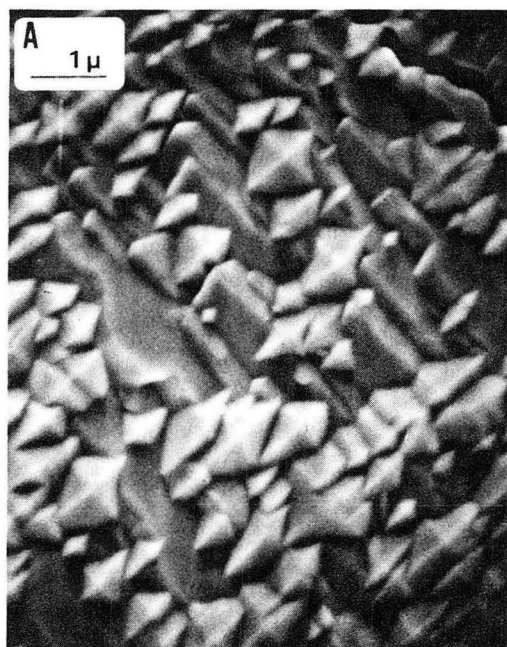
150 mtorr. The exit line was throttled for the second case to raise the pressure. The improvement in film properties for these two depositions is believed to be due to the low rf power (5 watts instead of 10 watts) and the lower oxygen flow rate (1.0 sccm instead of 8.0 sccm).

SEM photographs of the surface for the film deposited using the helium bleed stream are given in Figure 35. The surface was not completely uniform. Some of the areas look like Figure 35-A and have large crystals and a lot of the smaller diamond shaped crystallites. In other regions, like those shown in Figure 35-B, there are fewer of the diamond shapes and more of the larger crystallites. The surface structure for the throttled case is shown in Figure 35-C and follows the same type of behavior.

3.3.5 Titanium Substrates

Structural properties of plasma deposited titanium dioxide on titanium substrates are important in determining and explaining photoanode performance. Substrates used to measure the structural properties were the same as those used in fabricating the photoanodes -- polycrystalline titanium foil (grain sizes 15-20 microns in diameter) etched in hydrofluoric acid. Since the substrate was polycrystalline, many of the titanium diffraction peaks appeared in the x-ray diffraction measurements. To minimize possible confusion, the peaks caused by the titanium substrates are excluded from the diffraction patterns

Fig. 35. SEM of titanium dioxide deposited onto sapphire: crystallite growth enhancement: A. and B. same film but at different locations; deposited with helium bleed stream present, C. no helium bleed stream (see text).



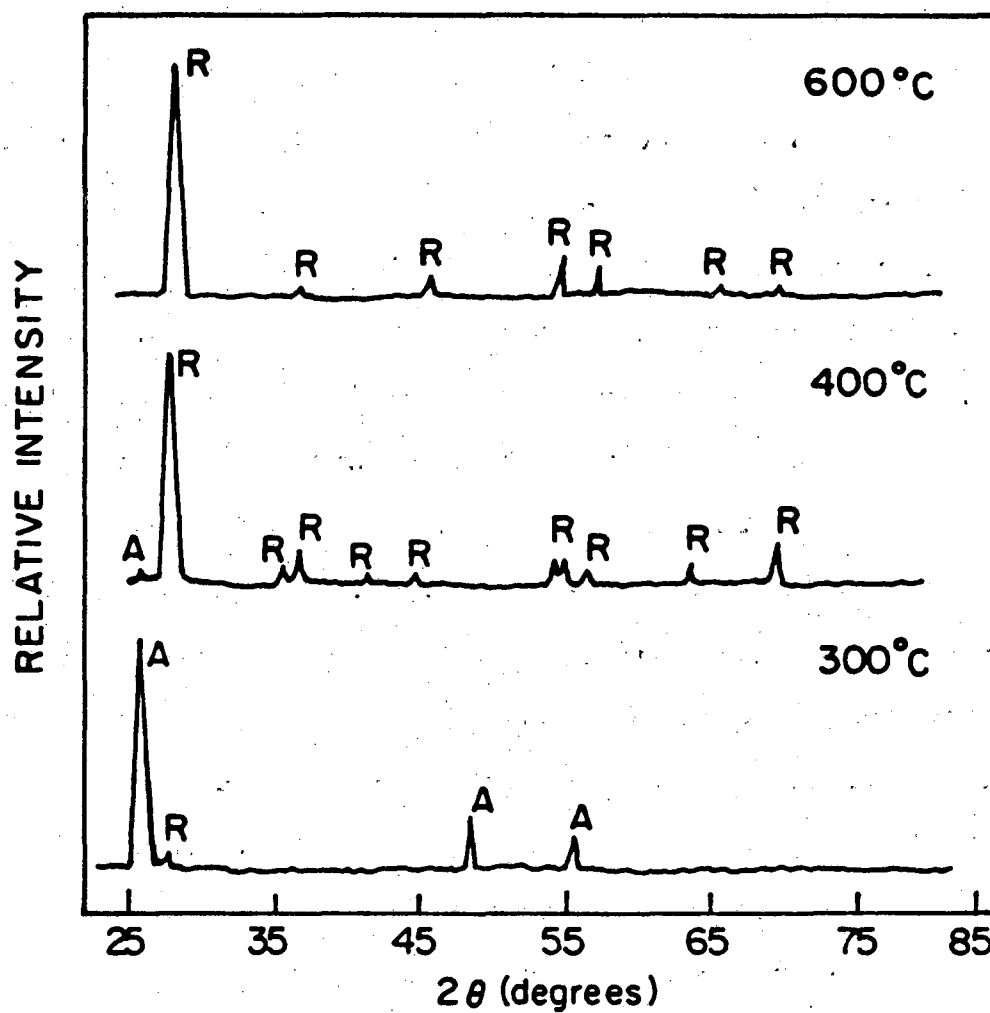
XBB 828-7396

Fig 35

reported here.

When films of titanium dioxide were deposited onto titanium substrates at 200 C, no x-ray diffraction peaks from the oxide were observed. At deposition temperatures of 300 C and higher, the oxide was polycrystalline. The x-ray diffraction properties are presented in Figure 36. The diffraction pattern for the 300 C deposit indicates the presence of the anatase modification and there is also one small peak which can only be caused by the presence of rutile. The amount of rutile present is small compared to the amount of anatase. For all the other substrate materials, rutile was not found to be present except for deposits made at 400 C or higher. Depositing the film at 400 C also gave a mixture of anatase and rutile, but in this case the amount of anatase was small, and the rutile was dominant. The x-ray diffraction properties for films deposited at 600 C indicated that rutile was the only form present.

In terms of growing rutile films, the titanium substrates seem to be superior to the other materials examined in this study. This is probably influenced by the small amount of oxide thermally grown on the titanium before the plasma deposition. This oxidation occurs at two points in the overall deposition process. First, there is some oxidation of the titanium substrate when it is placed on the heated lower electrode and is exposed to the atmosphere; the exposure time here is very short (1-2 minutes). Second,



XBL 828-6289

Fig. 36. X-ray diffraction spectrum: titanium dioxide deposited onto titanium (Cu k alpha radiation).

there is probably some further oxidation during the oxygen plasma descum (5 minutes, 10 watts, 150 mtorr). Titanium does not oxidize very rapidly particularly at low temperatures, and thus the oxides are thin (about 100 nm for the highest temperature cases).

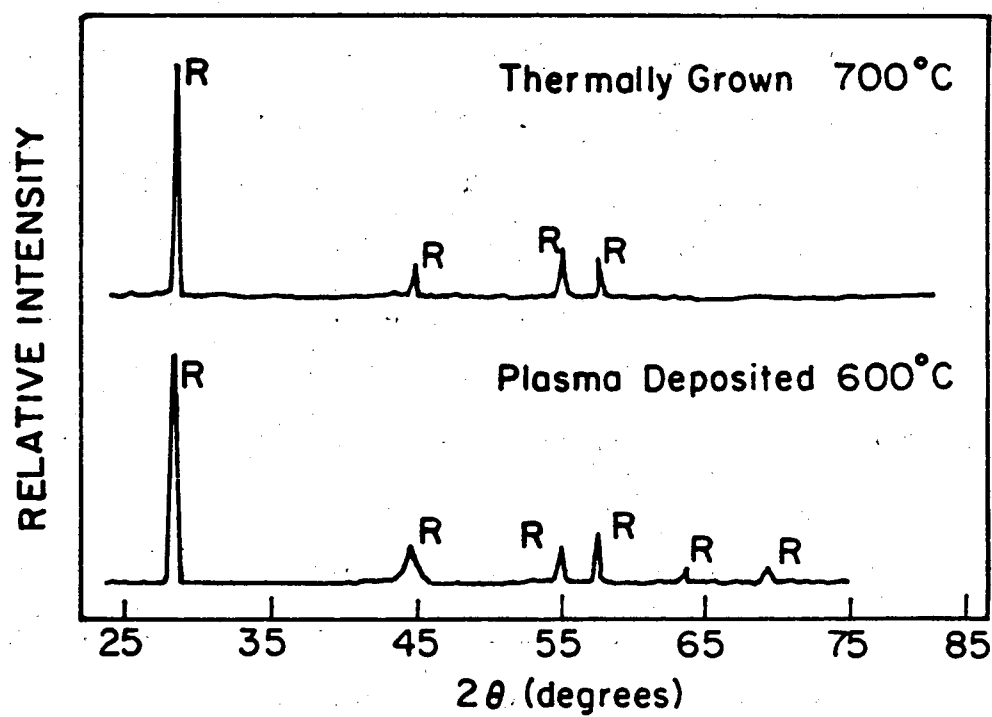
The structure of the thermal oxide is very important for subsequent film growth. Hass (10) reported that rutile resulted after oxidizing pure titanium in air at temperatures greater than 200 C (below 200 C he could not get reasonable films). He also stated that oxidation of titanium monoxide or titanium nitride, which occurs for the impure case, gives the anatase structure. According to Stringer (87) only the rutile modification of titanium dioxide has been found on titanium heated in oxygen. In view of those reports, the thermal oxides grown in this study should be rutile. A rutile surface should be the best surface for growing rutile in terms of lattice match and activation energies. Thus, it is reasonable that the titanium substrates have a higher preference than the other substrate materials for generating rutile films.

Another question to address is whether the rutile peak appearing in the diffraction pattern for the 300 C deposit is the result of plasma deposited rutile or simply the thermal rutile. At 300 C the amount of thermal titanium dioxide that can be grown within a few minutes is so small that a diffraction peak would probably be undetectable.

For the purpose of comparing thermally grown oxides to

the plasma deposited oxides, some of the titanium substrates were oxidized at 700 C with approximately 100 cc/min of oxygen. The x-ray diffraction patterns for a thermal oxide and for an oxide plasma deposited at 600 C are shown in Figure 37. In both cases the oxides appear to be of the rutile modification. The relative intensities of the two oxides are very similar except that the deposited film shows two additional peaks not given in the thermal oxide. The similarities in relative peak intensities for the two oxides are caused in part by the roughness of the surface of the titanium substrate. A very rough surface tends to make the crystallites in the oxide film appear randomly oriented on a macroscopic scale. Since x-ray diffraction is a macroscopic measurement technique, differences in preferred orientation may be hidden.

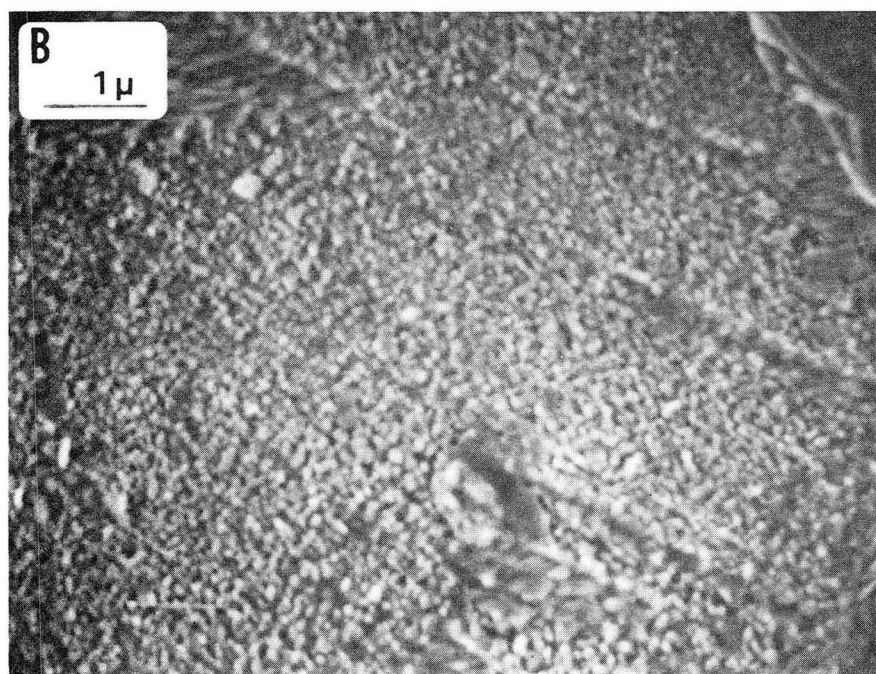
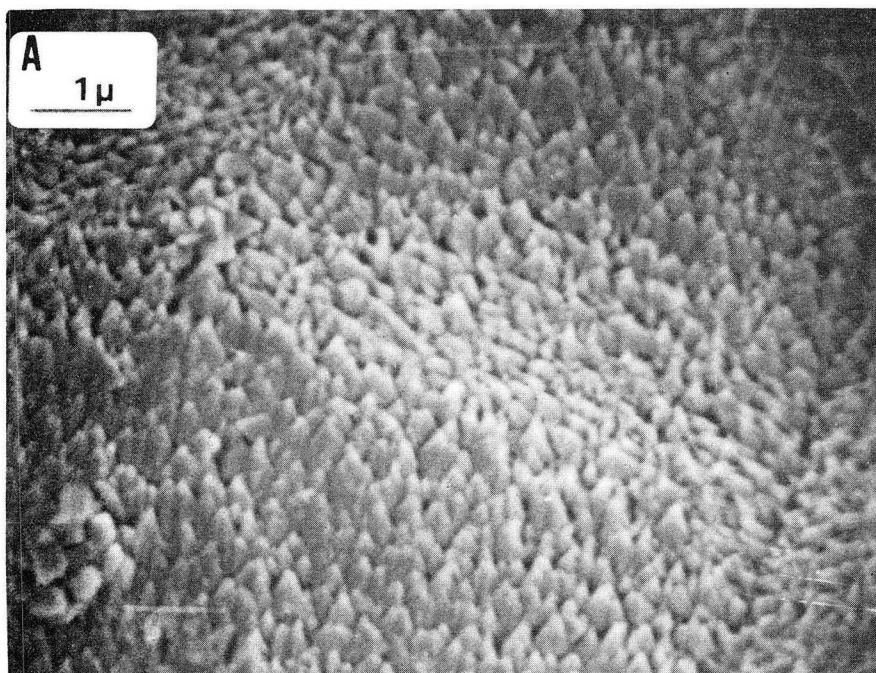
An examination of the thermal oxide and plasma oxide with a SEM reveals that there are significant differences in the grain structure. Figure 38 shows SEM photographs of the oxides on the surface of a single grain of the titanium substrate. It is apparent that the crystallites in the 700 C thermally grown oxide are smaller than those for the film plasma deposited at 600 C. The grains in the thermal oxide appear randomly oriented. But for the deposited film, the crystallites are growing up from the surface in columns. The growth for the film deposited on titanium is similar to the growth on the sapphire substrate.



XBL 828 - 6288

Fig. 37. Comparison of x-ray diffraction spectra: plasma deposited and thermally grown films (Cu K alpha rad.).

Fig. 38. SEM of titanium dioxide on titanium: A. plasma deposited at 600 C, B. thermally grown at 700 C.



XBB 828-7395

Fig 38

3.3.6 Plasma Deposited Film Structure Compared With Literature Results

Significant differences exist between the structural properties of the plasma deposited films prepared in this study and the properties reported in the literature. For example, amorphous films made by CVD tend to begin crystallizing at anneal temperatures of approximately 300 C while the plasma deposited films of this study remain structurally unchanged even at anneal temperatures of 400 C. The higher stability of the plasma deposited oxide could be caused by the difference in the types of impurities. The CVD films probably contain significant amounts of hydrogen and/or carbon while the plasma deposited film primarily has chlorine as the impurity (see Section 3.2).

The other major difference between the plasma deposited film and CVD films is the grain size. For the same substrate material and deposition temperature, the plasma deposited films had crystallites that were 3-4 times larger than those in films deposited by CVD (88) from titanium tetrachloride and oxygen. This difference in properties is believed to be due to ion bombardment caused by the plasma.

Other investigators have reported enhanced crystal growth and reduced epitaxial temperatures as a result of ion bombardment during the deposition process. Most of the work was reported for sputter deposition systems (93-96). There have also been some reports of reducing the epitaxial growth temperature of silicon (74,75), zinc oxide (72), and gallium

arsenide (73) by using plasma enhanced deposition. It is generally accepted that the plasma performs one or more of the following functions: (1.) bombards the surface of the substrate before deposition producing a cleaner surface that is more favorable for epitaxy, (2.) generates more nucleation sites and reduces the thickness at which complete film coverage occurs, and (3.) increases the surface mobility of the adsorbed species.

The change in film structure caused by the rf power level is also a topic needing further research. In the present study, the best films were obtained using the lowest rf power levels (0.06 watts per square centimeter). Hariu (73) reported getting epitaxial gallium arsenide films for a limited range of rf powers and polycrystalline films for power levels outside that range. Shiosaki (72) found that the highest rf power levels required the lowest temperatures for obtaining epitaxial zinc oxide films. The differences in the trends shown by those three systems suggest that the plasma is perhaps playing a different role for each case in improving the crystal growth.

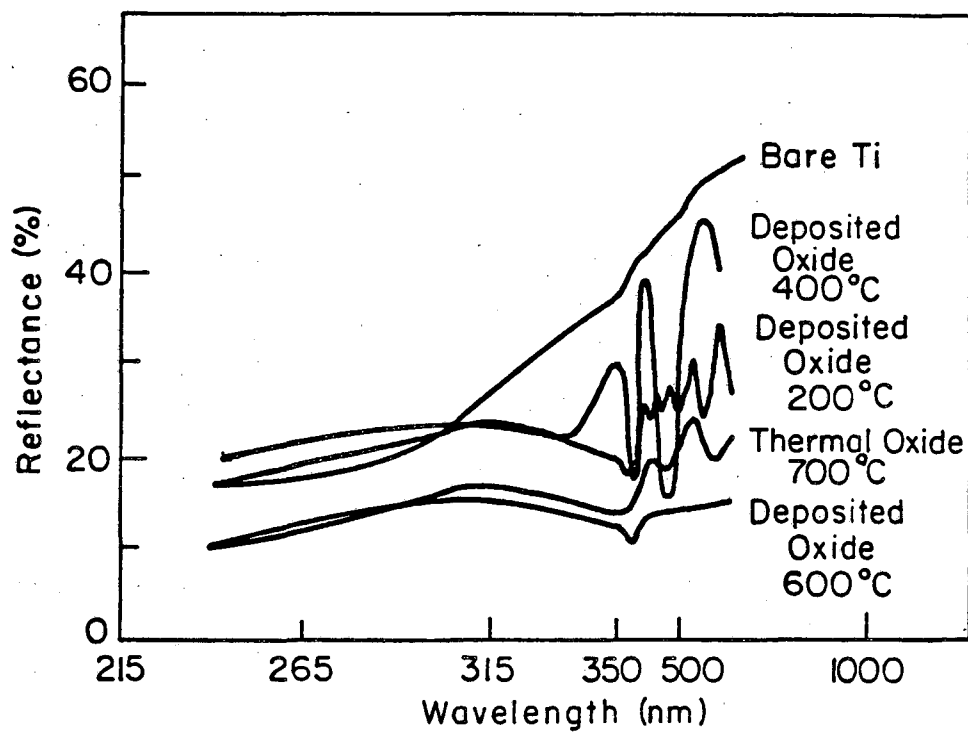
3.4 Optical Properties

The optical properties of titanium dioxide are important for many of the prospective applications of these films. Reflectance and transmittance properties were measured for some of the plasma deposited titanium dioxide films. The purpose was to compare the properties of the PED films to those made by other methods and to obtain information for use in explaining the photoelectrochemical properties.

Figure 39 illustrates the reflectance properties of some titanium dioxide films on titanium substrates. Three of the films were deposited at substrate temperatures of 200, 400, and 600 C with an oxygen flow of 45 micromoles per minute and a titanium tetrachloride flow of 40 micromoles per minute. The thermal oxide was grown by oxidizing the titanium substrate at 700 C in flowing oxygen. Results are also presented for the "bare" substrate (after HF etch).

The drop in reflectance for the "bare" substrate, as the wavelength decreases, is typical for metal surfaces (97). Ideally there is a discontinuous drop in reflectance when the frequency of the light becomes equal to the plasma frequency of the metal. The plasma frequency is proportional to the electron density and for metals occurs in the high visible or ultraviolet range.

An oxide on a metal surface gives the metal different reflectance properties because the optical properties of the



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Fig. 39. Reflectance properties.

oxide differ from those of the metal. The change in surface structure can also contribute to the change in reflectance. A smooth surface, of course, is more reflective than a rough one. Consequently, if the oxide is amorphous or has very small grains, the reflectance should be higher than for large grain oxides. (Note: The titanium grains in the substrate have diameters of approximately 15 to 20 microns and thus are much larger than the oxide crystallites. See the section on film structure, Section 3.3.5). This probably explains why the films deposited at 200 and 400 C have higher reflectance values than the film deposited at 600 C and the film thermally grown at 700 C. All of the films begin to show interference effects at the long wavelength end of the spectrum. The results presented here are in agreement with the data reported by Douglas and Pettit (98) for their thermally grown titanium dioxide films and bare titanium.

Notice that the reflectance for the 600 C plasma deposited film is slightly lower than that for the film thermally grown at 700 C. Here again, the difference is probably due to a slightly larger grain structure for the deposited film. Neglecting structural differences, the optical properties for a material can be determined from the real and imaginary parts of the complex refractive index (135). The complex refractive index is given by

$$\bar{n} = n + ik \quad (4.)$$

where n is the real part of the complex refractive index and k is the extinction coefficient. The reflectance, R , is given by

$$R = ((n-1)^2 + k^2) / ((n+1)^2 + k^2) \quad (5.)$$

for normal incidence radiation. The extinction coefficient determines the absorption coefficient, α . The equation for the absorption coefficient is

$$\alpha = 4\pi k / \lambda \quad (6.)$$

where λ is the wavelength. The absorption of a light beam passing through a medium is given by

$$A = 1 - \exp(-\alpha x) \quad (7.)$$

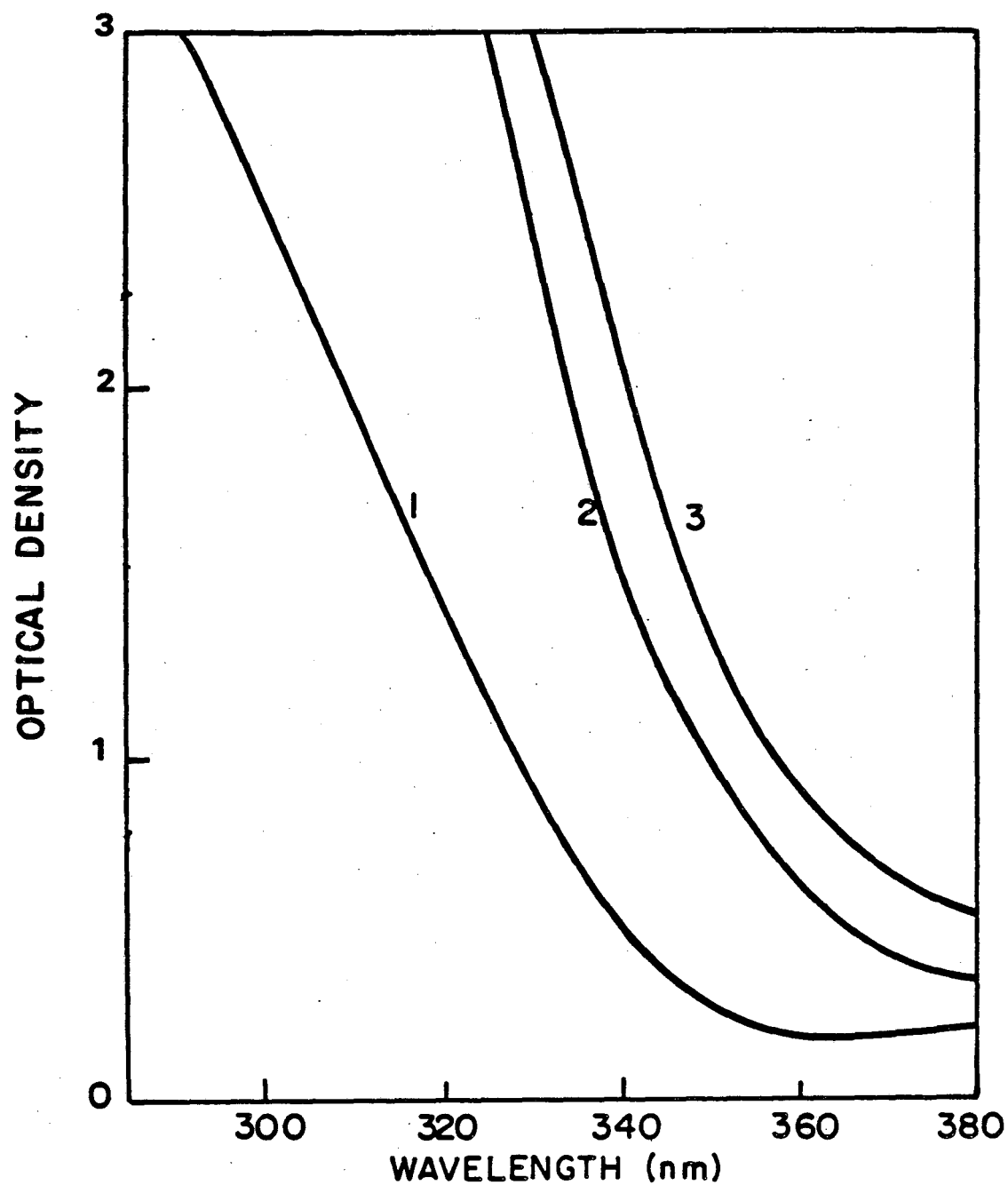
where A is the fraction absorbed and x is the distance into the medium.

It is necessary to consider whether the deposition temperature can change the refractive index to an extent that could explain the variation in reflectance. Based on the structural properties given in Section 3.3.5, the film deposited at 200 C is amorphous, the 400 C deposit is a mixture of anatase and rutile, and the 600 C deposit is pure rutile. The real part of the refractive index of rutile is

higher than that of anatase (Table 1), and an amorphous material usually has a lower refractive index than the crystalline form. According to Equation 5, the reflectance increases for high values of n . Thus the equation predicts (assuming constant k) a response that is the opposite of what was observed experimentally. Therefore the differences in reflectance resulting from the deposition temperature are due to differences in surface structure as stated earlier.

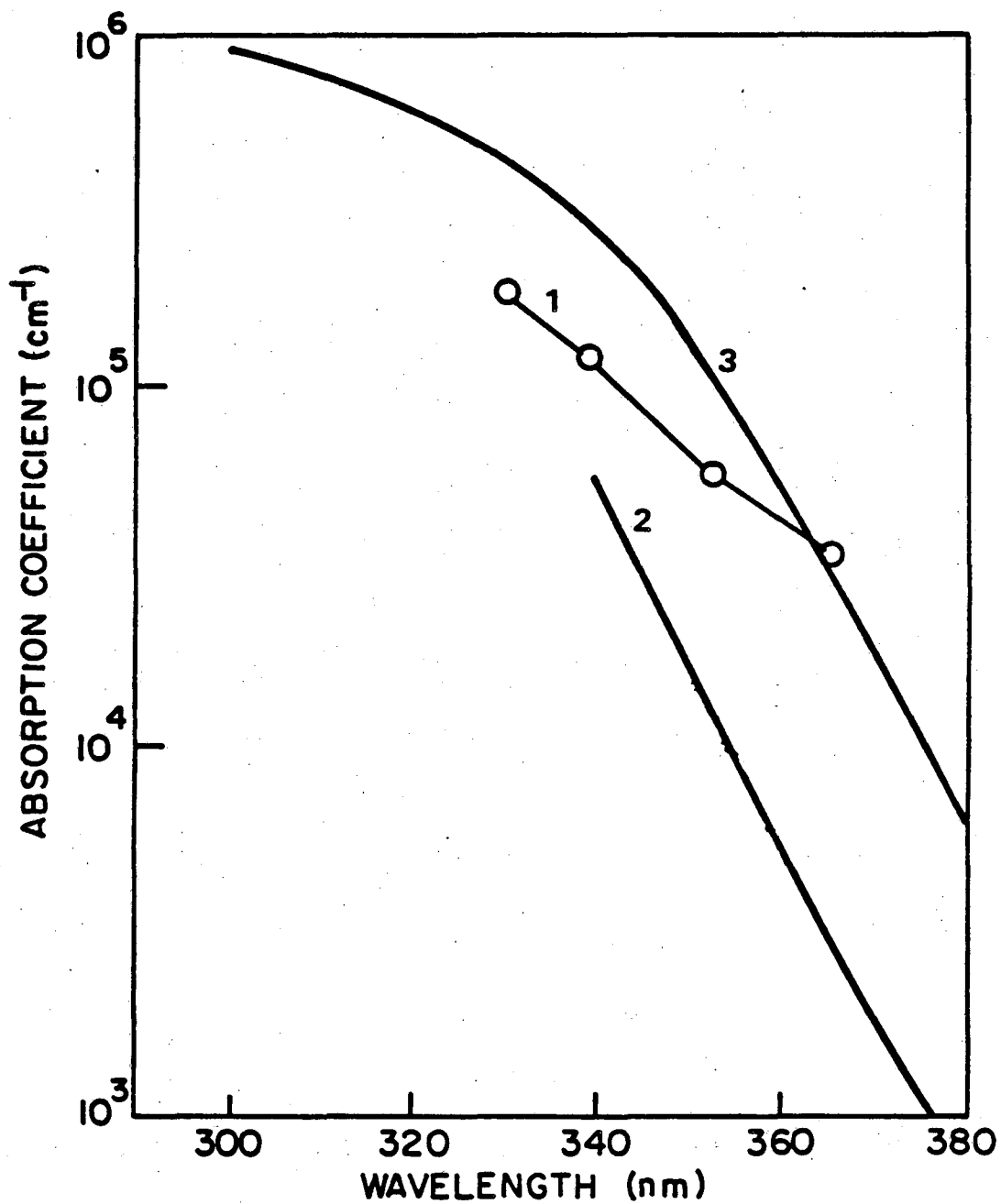
The transmittance as a function of wavelength is shown in Figure 40 for three of the deposited titanium dioxide films. The films were deposited at 600 C onto quartz substrates (2 mm thick). As expected, there is a smooth (no dips or bumps) variation in transmittance with increasing wavelength. However, the transmittance begins to level off at the longer wavelengths though it should continue to increase. This discrepancy is probably the result of not adequately accounting for differences in the reflectance for the substrate with a film on it and the blank substrate used as a reference.

To test further the accuracy of the data, the absorption coefficient was calculated for one of the deposited films and compared to the data reported in the literature. All of the information is presented in Figure 41. The absorption coefficient for the plasma deposited film are comparable to those reported by other investigators (91,99) even though no corrections were made for reflectance. Since the reflectance effects were neglected,



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Fig. 40. Transmittance properties of plasma deposited titanium dioxide films: 1. 120 nm thick, 2. 270 nm thick, 3. 420 nm thick. Optical density = $-\log(\text{Transmittance})$.



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Fig. 41. Absorption coefficients: 1. plasma deposited titanium dioxide, 2. from Mollers et al. (91), 3. from Eagles (99).

the actual absorption coefficients for the plasma deposited film are lower than that indicated in Figure 41 and, thus, are closer in magnitude to the results reported by Mollers et al. (91). Mollers et al. did not describe how they obtained their data but merely stated the results. The data obtained by Eagles (99) are also shown. Those results are from a theoretical calculation of the absorption coefficient and tend to over predict the experimental results.

Thus, the plasma deposited films seem to have optical properties similar to those for titanium dioxide made by other methods.

3.5 Electronic Properties

3.5.1 Silicon Substrates

Electronic properties of titanium dioxide have been studied for a variety of applications. In most studies, the dielectric constant is the most important property. The dielectric constant of crystalline titanium dioxide is unusually high; rutile has a dielectric constant of 180 along the c-axis, 89 along the a-axis, and a value of 110-117 for randomly oriented polycrystalline samples (27). Powdered anatase has a dielectric constant of 48 (27). By comparison, silicon dioxide and aluminum oxide have dielectric constants of 4 and 7 respectively (93). The other important property of interest is the electrical conductivity. Both of these properties are important in determining the performance of the plasma deposited titanium dioxide as a photoanode.

The high dielectric constant of titanium dioxide suggests that this material may be suitable for capacitor structures in microelectronic devices (2,11,89,100,101). The high refractive index of titanium dioxide makes it of interest as an antireflection coating for photovoltaic systems (4,5,102). In both applications the electronic properties of the titanium dioxide and the interface between silicon and the titanium dioxide are important in determining the overall performance of the devices. To test the suitability of the plasma deposited oxides for the above

applications and to obtain information on the electronic properties, capacitance - voltage properties were measured on films deposited onto silicon substrates. In these measurements titanium dioxide is considered an insulator and high resistivities are desired. Electrical contact to the oxide was made either with evaporated aluminum electrodes or with a mercury probe.

Detailed descriptions of the capacitance-voltage technique for analysis of metal-oxide semiconductor (MOS) systems have been presented in the literature (103-105). The capacitance of a metal - oxide - semiconductor capacitor is given by equation (8)

$$C = (C_{ox}^{-1} + C_{sc}^{-1})^{-1} \quad (8.)$$

where C is the total capacitance, C_{ox} is the oxide capacitance, and C_{sc} is the capacitance of the semiconductor space charge region. The thickness and the capacitance of the space charge region are voltage dependent. An idealized plot of the total capacitance, C , as a function of voltage is shown in Figure 42. When a space charge region is present in the semiconductor, the device is said to be in depletion. The minimum of the curve occurs when the space charge region is at maximum thickness. The maximum C occurs when the semiconductor is in accumulation (i.e. majority carriers are attracted to the surface), the space charge capacitance is infinite, and C is equal to the oxide

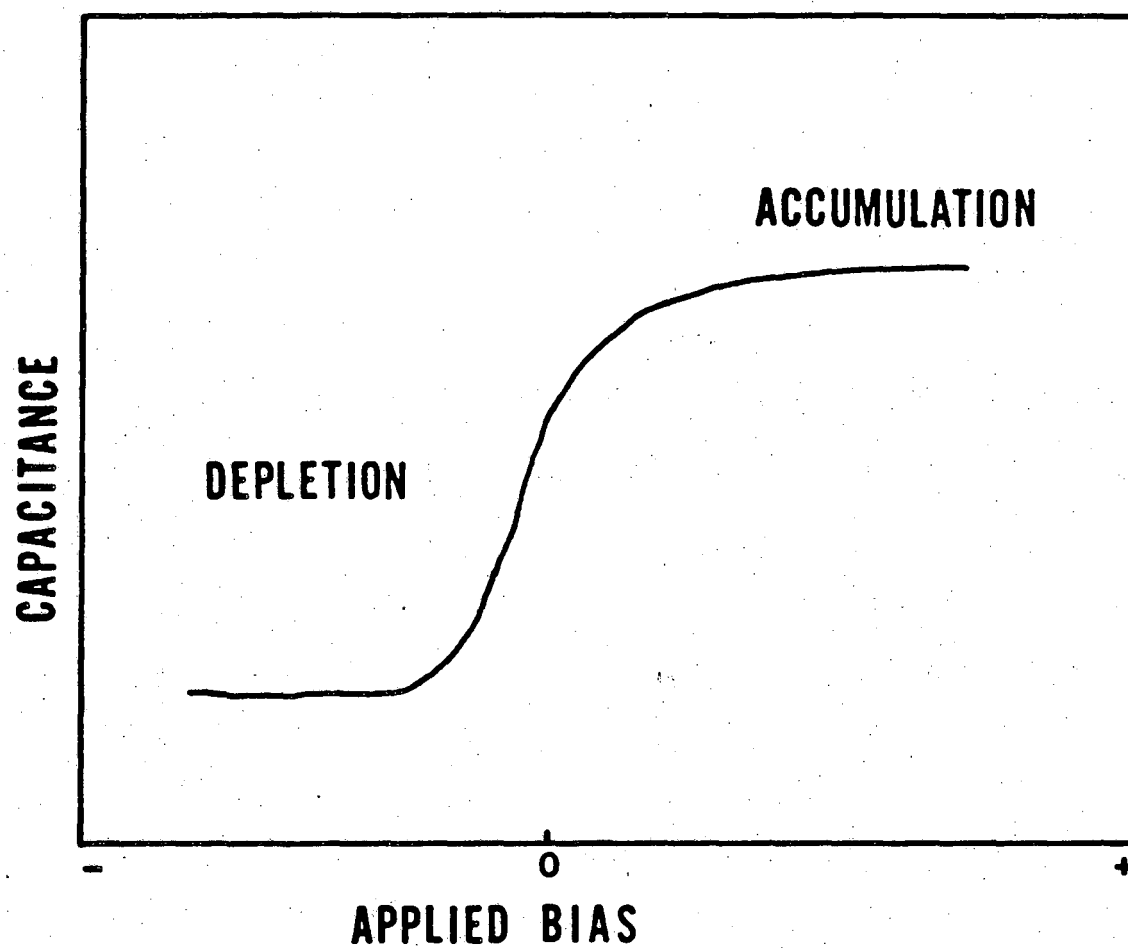
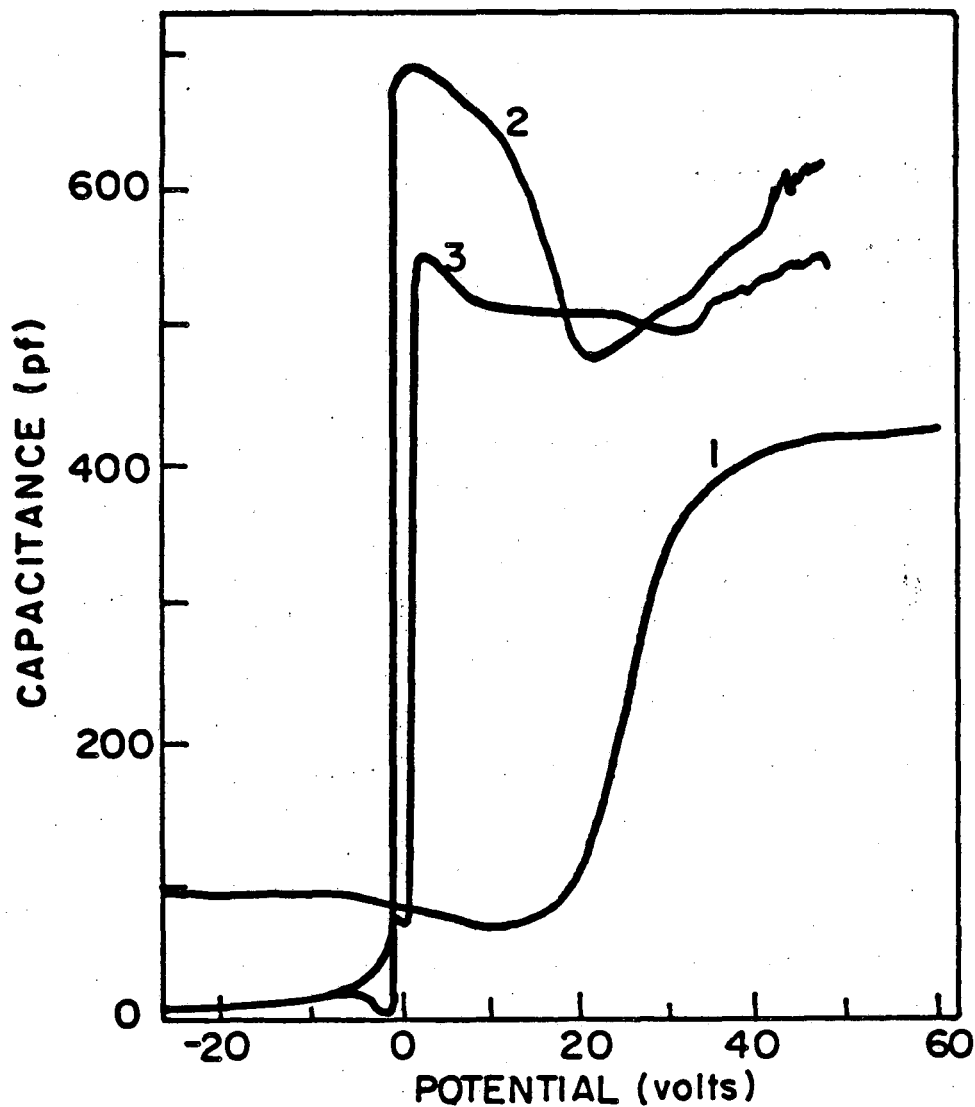


Fig. 42. Ideal C-V plot: n-type silicon.

capacitance.

In this study, n-type silicon wafers were used; therefore accumulation requires a positive bias on the metal contact to the titanium dioxide. The capacitance-voltage (C-V) plot for a titanium dioxide film that was plasma deposited at 250 C is shown in Figure 43. Curve 1, for the "as deposited" film, is representative of the curves usually obtained for deposition temperatures of 200-250 C. Dielectric constants for films deposited at those temperatures range from 25 to 30. The position of the curve on the voltage axis indicates that negative charge is present in the titanium dioxide. The origin of this charge is most likely chlorine ions incorporated during the deposition.

Annealing the films deposited at 200 to 250 C causes dramatic changes in their C-V characteristics. Curves 2 and 3 in Figure 43 are for sections of a film that was deposited at 250 C and then annealed in oxygen and argon respectively at 400 C. The changes that occurred seemed to be mainly caused by high temperature rather than by the gas used. After the anneal, the voltage required to switch the silicon from depletion to accumulation is reduced. This also indicates that the amount of trapped negative charge (chlorine ions) in the film has been reduced. The C-V behavior for the accumulation region, or rather what is believed to be the accumulation region, is strange. In accumulation, the capacitance should be a constant equal to



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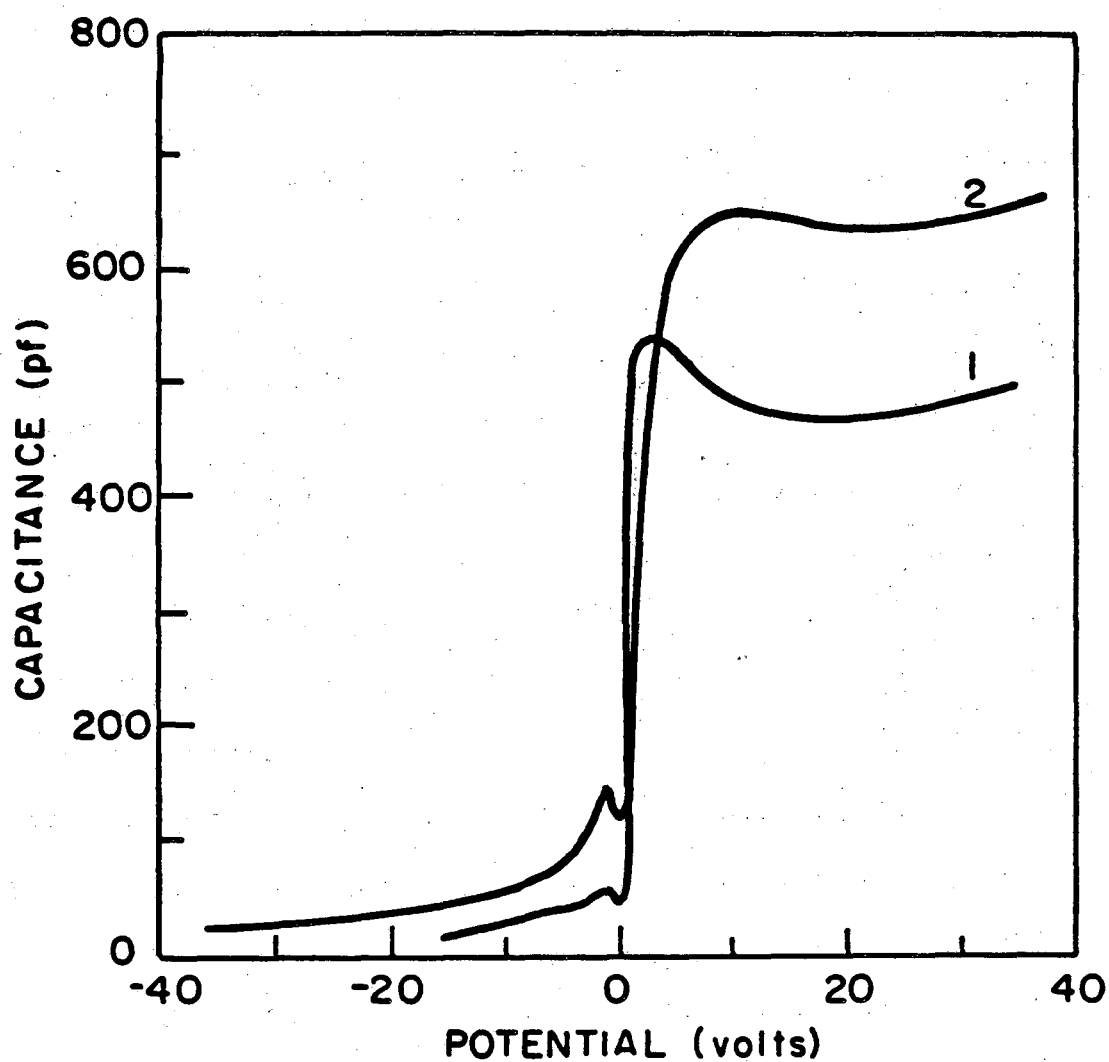
Fig. 43. C-V plots for titanium dioxide deposited onto silicon at 250 C: 1. as-deposited, 2. after annealed at 400 C in oxygen for 20 min., 3. after annealed in argon at 400 C for 20 min.

the oxide capacitance. However, the capacitance for the annealed films continues to vary with the applied voltage.

C-V plots were also recorded for films deposited at 400 C and 600 C. Plots for two of those films are given in Figure 44; they are similar in shape to the curves measured for the annealed films discussed above. The capacitance begins to decrease after reaching accumulation. However, the curve for the 600 C deposit seems more stable than the annealed films and the 400 C deposit.

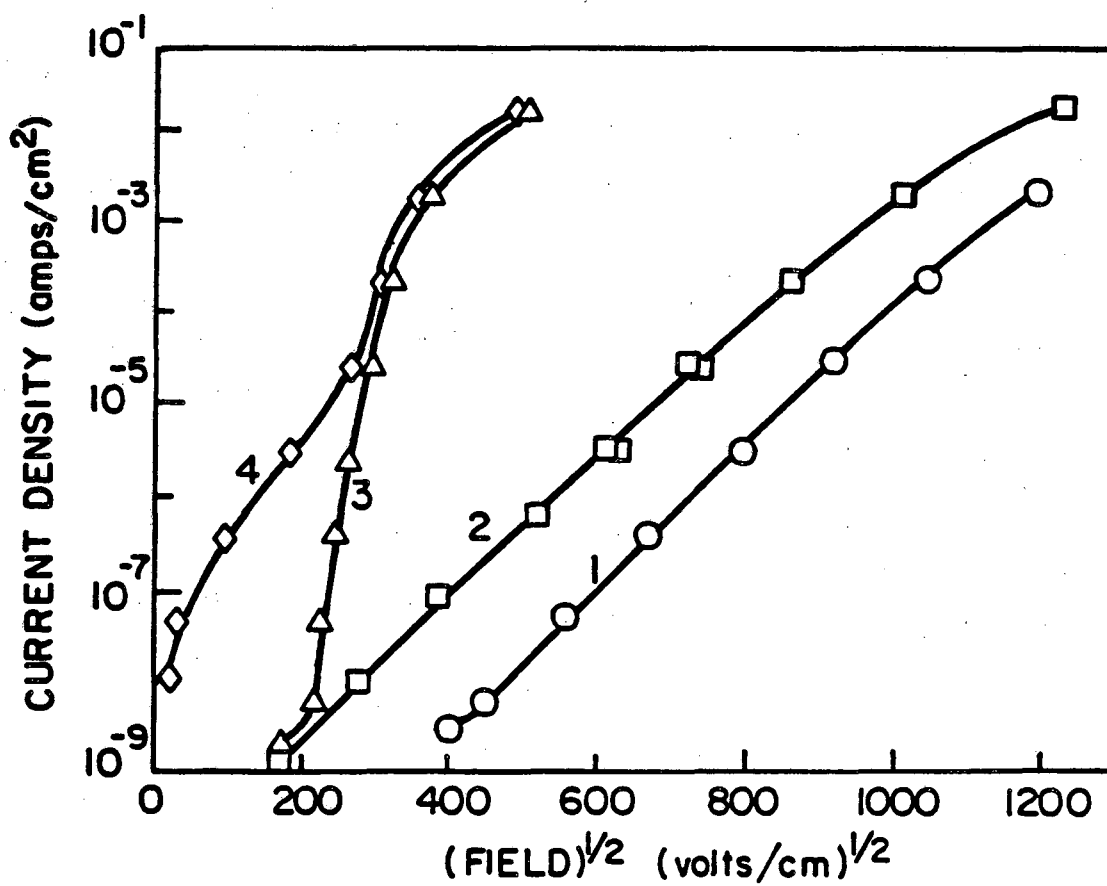
Current-voltage (I-V) properties for some of the films discussed above were also measured. Measurements for four of the films are presented in Figure 45 as Schottky plots (log current density vs the square root of the applied electric field). The film deposited at 200 C has the lowest conductivity followed by the 250 C deposit; Schottky plots for those two films are reasonably straight lines with approximately equal slopes. Annealing the 200 C deposit at 400 C in oxygen leads to a very large increase in conductivity. The concurrent change in slope also implies a change in the conduction mechanism. At higher fields, the Schottky plot for the annealed film is almost identical to that for the film deposited at 400 C. Thus, the change in current-voltage properties is analogous to the change in the capacitance voltage properties.

Results for the present study show that the two main differences between the films deposited at 200 C and those deposited at 400 C and higher are the structural properties



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Fig. 44. C-V plots for titanium dioxide deposited onto silicon at: A. 400 C, B. 600 C.



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Fig. 45. Schottky plots for titanium dioxide deposited onto silicon: 1. deposited at 200 C, 2. deposited at 250 C, 3. deposited at 400 C, 4. deposited at 200 C then annealed at 400 C in oxygen.

and the chemical composition. Based on the structural properties presented in Section 3.3.3, the 200 C deposit is amorphous while the 400 and 600 C deposits are polycrystalline mixtures of anatase and rutile. Capacitance and conductivity for titanium dioxide both depend on the structural properties. However, according to the results in Section 3.3.1, annealing the 200 C deposits at 400 C does not change the film structure. It remains amorphous, but the electronic properties do change. Film composition results presented in Section 3.2 show that the films deposited at 200 C and then annealed and the films deposited at 400 and 600 C contain less chlorine than the film deposited at 200 C. These differences in chlorine concentrations match the differences in electronic properties for the films.

Electrical conductivity of a material is determined by the concentration of conduction electrons and by the electron mobility. For metal oxides, the electron concentration can be increased by generating oxygen vacancies or metal interstitials (106), since both defects are electron donors. Conductivity in titanium dioxide has been reported to be the result of oxygen vacancies (24,34). Thus, the higher conductivity for the polycrystalline plasma deposited films is probably caused by the higher electron concentration induced by the oxygen vacancies. Adding another element to a material can increase or decrease the electron concentration. The change depends on the valence

of the element and how it is incorporated. Films deposited at 400 and 600 C have little or no chlorine, and so their electronic properties are almost solely determined by the oxygen vacancy concentration.

According to the results in Section 3.3, films deposited at 200 C are amorphous. The open structure of amorphous materials allows accommodation of relatively large (a few atomic %) amounts of impurity elements (107) before phase segregation starts. This property, coupled with the relatively low deposition temperature, allows sufficient chlorine to be incorporated into the films to alter the electronic properties. The chlorine in the films probably acts as an electron acceptor. As a result, the total concentration of electrons is equal to the number donated by the oxygen vacancies minus the number taken up by the chlorine acceptors. If the oxygen to titanium ratios are about equal for the 200 C deposit and the higher temperature deposits, then the 200 C deposit should have a lower conductivity. That is what is observed. Furthermore, annealing the 200 C deposits removes the chlorine. Consequently, the concentration of conduction electrons increases and so does the conductivity.

The presence of the chlorine in the film helps to compensate for the oxygen vacancies and improves the dielectric properties. That is why the films deposited at 200 C have fairly well behaved C-V plots. However, the films with the higher conductivities (i.e., essentially no

chlorine) are more semiconducting than insulating. As a result, the C-V characteristics are probably influenced by the depletion layer in the silicon and that in the titanium dioxide. Further studies are needed in order to obtain a complete explanation of these phenomena.

3.5.2 Titanium Substrates

Table 7 summarizes the electronic properties measured for four films plasma deposited onto titanium substrates. Before the electronic measurements were carried out, the photoelectrochemical properties were recorded (see Section 3.6.8). Thus, the electronic properties should be representative of these photoanodes (this will be discussed further in Section 3.6).

All four films have very high dielectric constants (averaging 160). As stated in Section 3.5.1, the dielectric constant for rutile is 180 along the c-axis and is 110-117 for rutile with randomly oriented crystallites. The fact that the plasma deposited films have such a high dielectric constant implies that the crystallites have a high degree of preferred orientation along the c-axis.

Table 7. Electronic Properties For Plasma Deposited Titanium Dioxide On Titanium Substrates

Deposition Conditions: 600 C, 360 micromoles oxygen per minute, 40 micromoles titanium tetrachloride per minute

RF Power (watts)	Thickness (microns)	Dielectric Constant	Resistivity (megohm-cm)
5	1.5	166	0.9
10	1.2	162	1.0
10	1.3	158	2.2
20	1.3	157	.60

3.6 Photoelectrochemical Properties

3.6.1 Establishing A Photoanode Reference

For this study, it was desired to have a photoanode, not plasma deposited, that could be used for a direct comparison of performance. Single crystal rutile could have been obtained, but it is expensive. In addition, it is very difficult to make high quality single crystal rutile photoanodes (22). There have been some reports in which the performance of single crystal rutile photoanodes were compared with films of titanium dioxide grown on a titanium substrate with a gas burner or in a furnace (6,43). The thin films were found essentially equivalent in photoelectrochemical performance to single crystal photoanodes. In view of that information and of the simplicity of thermally growing the oxides, thermally grown photoanodes were fabricated and used in this study for comparison with the plasma deposited oxides. At first, the films were grown by oxidizing the titanium substrates in a bunsen burner. It was very difficult to obtain films with reproducible photoelectrochemical properties using this method. Some of the films gave good photoresponses, but most of them showed low photocurrents.

In an effort to get photoanodes with more consistent properties, some of the titanium substrates were oxidized in a quartz tube furnace with oxygen. After the oxidation, the films were then reduced in a mixture of 90% helium and 10%

hydrogen. Various oxidation and reduction conditions were examined. In general, the thicker films, grown for 1 to 2 hours, did not work as well as the thinner oxides, grown for 0.25 to 0.5 hours. Increasing the conductivity of the thicker oxides by reducing them for longer times than the thinner oxides still did not bring their performance up to that for the thinner oxides. In fact, long reduction times (1.5 hours) caused a decrease in the photoresponse. The best thermally grown photoanodes were obtained by oxidizing the titanium at 700 C for 0.5 hours in 100 cc/min of oxygen and then reducing for 0.5 hours in a 90% helium 10% hydrogen mixture at 100 cc/min at 600 C. Therefore, unless otherwise indicated, all references to thermally grown titanium oxides in this thesis will be to films grown under these conditions.

3.6.2 Deposited Film Performance: Early Trials

The first set of plasma deposited photoanodes was fairly thick (greater than 5 microns) and, like the thick thermally grown photoanodes, gave a very poor photoresponse. The film performance increased when the thickness was reduced. Various deposition temperatures were also examined. In general, the films deposited at 200 to 300 C did not work as well as those deposited at 400 and 600 C. This is believed to be due to differences in crystallinity; the higher temperature films have larger grains. Therefore, most of the plasma deposited photoanodes were made at 600 C.

This deposition temperature yields films of the rutile structure (see Section 3.3.5, Film Structure). The thermally grown anodes are also rutile, and most of the work reported in the literature is for the rutile form of titanium dioxide. Thus, the films deposited at 600 C are considered to be the simplest base for comparison with titanium dioxide photoanodes made by other techniques.

A brief examination was also made of the changes in the photoelectrochemical performance of plasma deposited anodes which received a post-deposition hydrogen anneal. Two depositions were performed at substrate temperatures of approximately 600 C. In both cases, two titanium substrates were used; two of the films, one from each deposition, were used to fabricate photoanodes. The other two were reduced in a 90% helium 10% hydrogen mixture (100 cc/min) at 600 C for 0.5 hours. After the reduction, they were also made into photoanodes. The photocurrent as a function of voltage was measured for all four anodes using the full output (white light) from the ultraviolet lamp. For both depositions, the photoresponse for the films that were reduced was approximately a factor of three lower than that for the corresponding unreduced films. The reduced film also had a higher dark current which implied a higher conductivity. The higher conductivity causes a reduction in the thickness of the depletion region. As a result, less absorbed light contributed to the photocurrent, and the overall performance was decreased.

3.6.3 Gas Ratio

Various titanium tetrachloride to oxygen ratios were examined during deposition in order to optimize the photoelectrochemical properties. This series was performed by varying the titanium tetrachloride flow over a range of 40 to 60 micromoles per minute and keeping the other deposition parameters fixed. The other parameters were 45 micromoles of oxygen per minute, 10 watts rf power, a substrate temperature of 600 C, a deposition time of 7 minutes, and a pressure of 150 mtorr. Of course, the residence time also changed and so did the deposition rate. Photocurrents as a function of voltage were measured for the films using the full output from the ultraviolet lamp.

Photoresponses for three of the plasma deposited anodes and one of the furnace grown anodes are shown in Figure 46. Dark currents for all four cases were essentially zero when compared to the photocurrents. Curves for the deposited films are all very similar in shape; photocurrent onset occurs at about the same voltage, and the initial slopes are similar. However, as the higher potentials are approached, there is a significant difference in the photocurrents for the film deposited with the lowest oxygen to titanium tetrachloride ratio. At an anode potential of 2.5 volts vs SCE, the photocurrent for the deposited films are 5.4, 6.1, and 6.3 mA/sq cm for oxygen to titanium tetrachloride ratios of 0.72, 1.0, and 1.1 respectively. As stated earlier, the

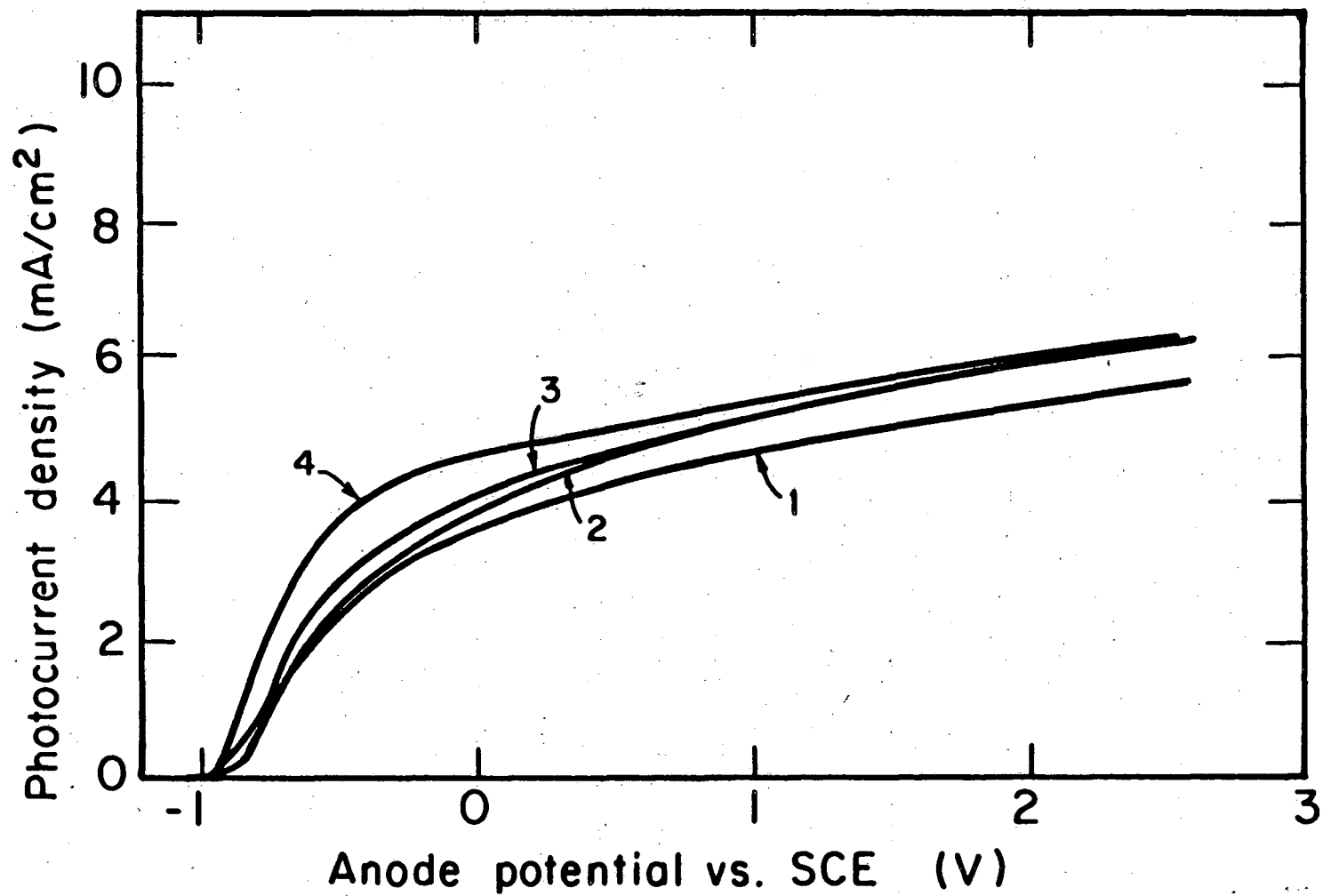


Fig. 46. Photocurrent - voltage comparison for titanium dioxide: 1. deposited 1.8 microns thick, 2. deposited 1.2 microns thick, 3. deposited 0.9 microns thick, 4. thermally grown.

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deposition rates for the films were different and so are the final thicknesses. The order of increasing photocurrents is also the order of decreasing thicknesses; the thicknesses are 1.8 microns, 1.2 microns, and 0.9 microns respectively. At this point it is unclear whether the thickness is a more important factor than the feed gas ratios. Further discussion of this matter will be presented in Section 3.6.5 and 3.6.9.

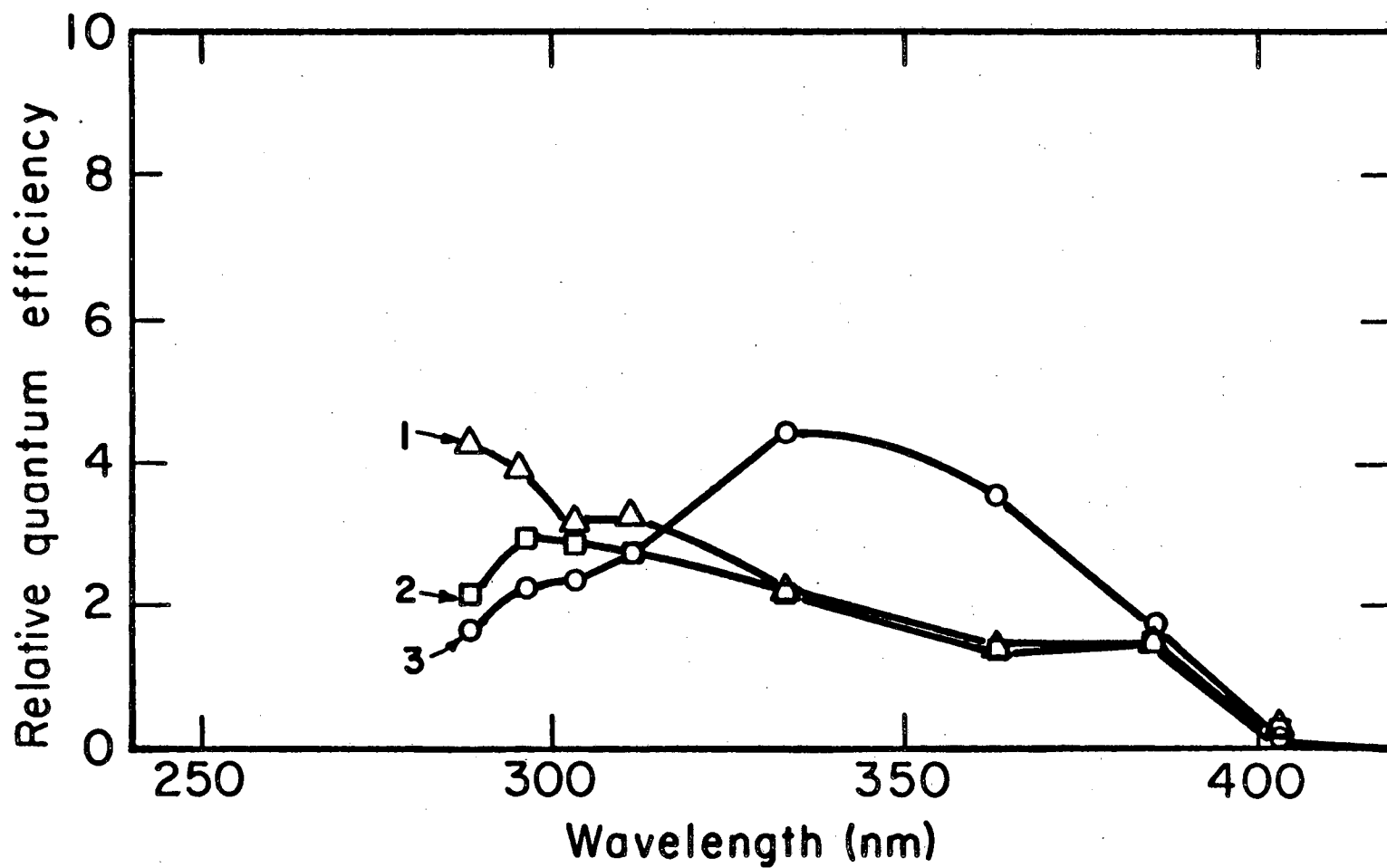
The photocurrent for the thermally grown anode shows a significantly sharper rise with voltage than the plasma deposited photoanodes. Yet, the peak photocurrent, at high voltages, for the thermally grown anode is approximately equal to that for the best two plasma deposited photoanodes.

Flatband voltages for the thermally grown anode and for two of the plasma deposited anodes were also compared. The flatband voltages were estimated by assuming that they were equal to the potential at which the photocurrent onset occurs. This method has been found to give flatband potentials that are comparable to those obtained by capacitance techniques (108). The principles behind this method are fairly simple. At the flatband potential, the electronic energy bands are flat through the bulk of the semiconductor to the surface. In the absence of the depletion region, the photogenerated electrons and holes can not be separated. Thus, they recombine and give a photocurrent of zero. By this method, the thermally grown photoanode described above had an anodic photocurrent onset

at -1.00 volts vs SCE while the best two plasma deposited anodes had values of -0.97 and -0.96 volts vs SCE. These values are slightly lower than the usual value of -0.9 volts vs SCE (56) for rutile.

Current - wavelength properties for the three films discussed above were also measured. The measurements were made with the photoanodes at +0.125 volts vs SCE and at a scan rate of 100 nm/min. Figure 47 summarizes the measurements in the form of relative quantum efficiency as a function of wavelength. As indicated previously, the plasma deposited films display curves with similar shapes. There is, however, some deviation between them at shorter wavelengths (311 nm and less). Also, there is a very large difference between the response for the thermally grown film and the plasma deposited films. The quantum efficiencies for the deposited films and the thermally grown film are approximately equal for the long wavelengths (380-400 nm). In the intermediate wavelength range (315-380 nm), the quantum efficiencies for the thermally grown photoanode are significantly higher than those for the two plasma deposited photoanodes. But, the quantum efficiencies for the plasma deposited photoanodes are significantly higher than those for the thermally grown anodes at the shorter wavelengths (less than 315 nm).

The shape of the photoresponse - wavelength curve depends on many factors such as light absorption characteristics, electronic properties, bulk recombination,



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Fig. 47. Relative quantum efficiency - wavelength response:
1. & 2. deposited anodes, 3. thermally grown.

surface recombination, and film thickness. For this study, the film thickness is small enough to be a very important factor. Absorption coefficients decrease as the wavelength is increased. As a result, a thick film should have its peak photoresponse at longer wavelengths than a thinner film. The thinner film is unable to absorb significant amounts of the longer wavelengths so the peak photoresponse is shifted toward the shorter wavelengths. There have been reports of a drop in the photoresponse at the shorter wavelengths for some semiconductor electrodes (13) including titanium dioxide anodes. This type of behavior can give a bell shaped photoresponse similar to that for the thermally grown film and also similar to the results for simple photoconductivity measurements (36). The drop is usually attributed to surface recombination (13,15,51) since most of the light is absorbed in the near-surface region.

Although the thickness of the thermally grown film is unknown, it is believed to be thinner than the two plasma deposited films. Thus the response peak for the thermally grown photoanode should occur at a shorter wavelength than the deposited anodes. Instead, the opposite is true; the response for the thermally grown anode has its peak at a longer wavelength. Part of this behavior is probably caused by the difference in band bending properties for the thermally grown anode and the deposited anodes.

The photoresponse at the shorter wavelengths (less than 315 nm) for the deposited films is better than that for the

thermally grown anode. None of the photoresponse measurements were corrected for possible reflectance differences. However, the reflectance properties for the thermally grown titanium dioxide films and the plasma deposited titanium dioxide films were compared in Section 3.4, Optical Properties. Based on those results, the reflectance for the titanium dioxide films plasma deposited at 600 C are within two percent of the values for titanium dioxide films thermally grown at 700 C. Thus the differences in wavelength response for the thermally grown anodes and the plasma deposited anodes cannot be attributed to differences in the reflectance.

3.6.4 RF Power And Photoelectrochemical Performance

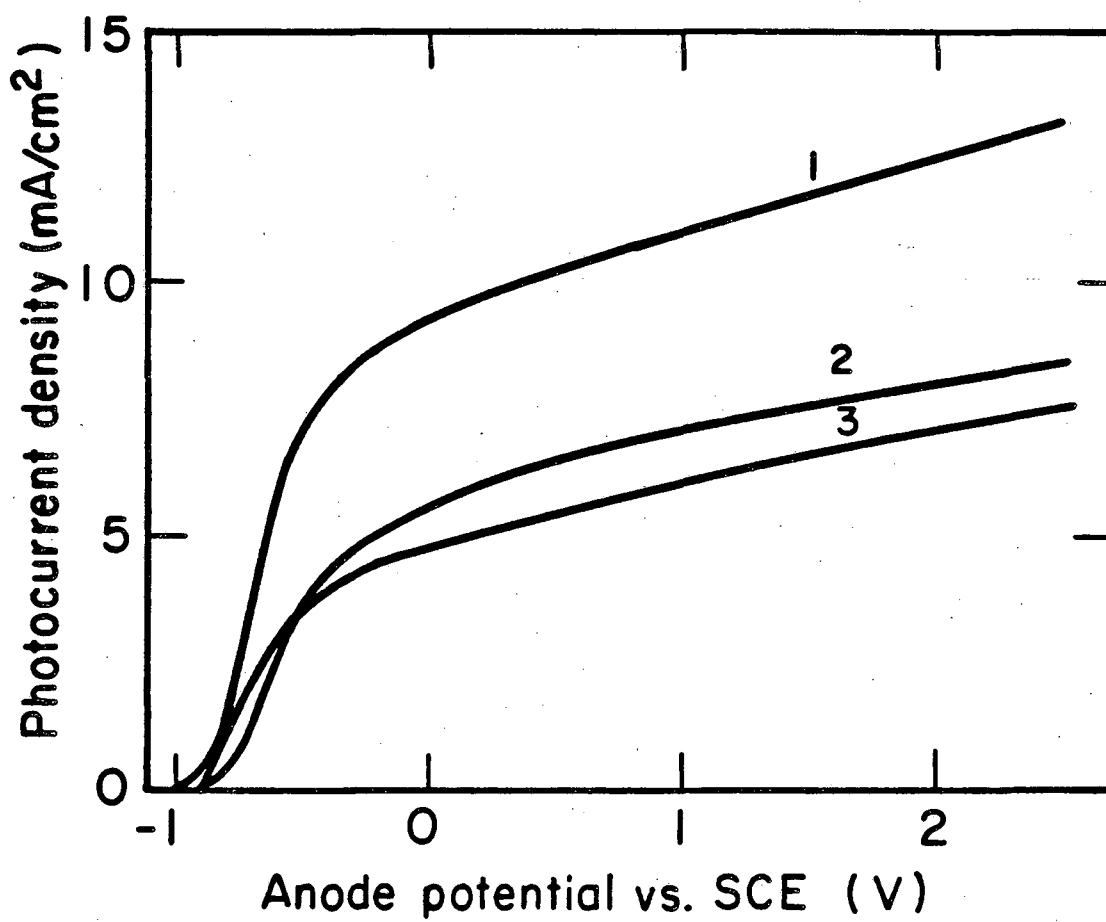
The dependence of the photoelectrochemical properties of plasma deposited titanium dioxide on rf power was also examined. As shown in Section 3.3.4, Film Structure, the film structure is a function of rf power. Also, ion bombardment, being a function of the rf power, can alter the surface composition and perhaps create surface states unobtainable by other methods. For this series, only the rf power was varied. The results from the previous series indicated that the photoelectrochemical properties may be favored by high ratios of oxygen to titanium tetrachloride for the feed gases. So, for this series, the oxygen flow was increased to 8 sccm, 360 micromoles per minute. The deposition time and temperature were 15 minutes and 600 C,

and the titanium tetrachloride flow rate was 40 micromoles per minute.

Figure 48 illustrates the photocurrent - voltage properties for three titanium dioxide films deposited at rf powers of 10, 100, and 200 watts. The deposition rate also varied with power; the film thicknesses were 1.15 microns, 0.79 microns, and 0.95 microns, respectively, for the increasing rf powers. The films deposited at 10 watts have a much higher photocurrent than do the films deposited at higher power levels. The difference in the performance is too large to be completely accounted for by differences in thickness, although this is a contributing factor. Further evidence that the thickness is not the only factor in such differences can be seen by a comparison of the photocurrents for the 100 watt and the 200 watt depositions. The 100 watt deposit has a higher photocurrent than the 200 watt deposit, yet the 100 watt film is the thinner of the two deposits. Thus, there must be other factors, induced by the rf power level, which determine the photoelectrochemical properties.

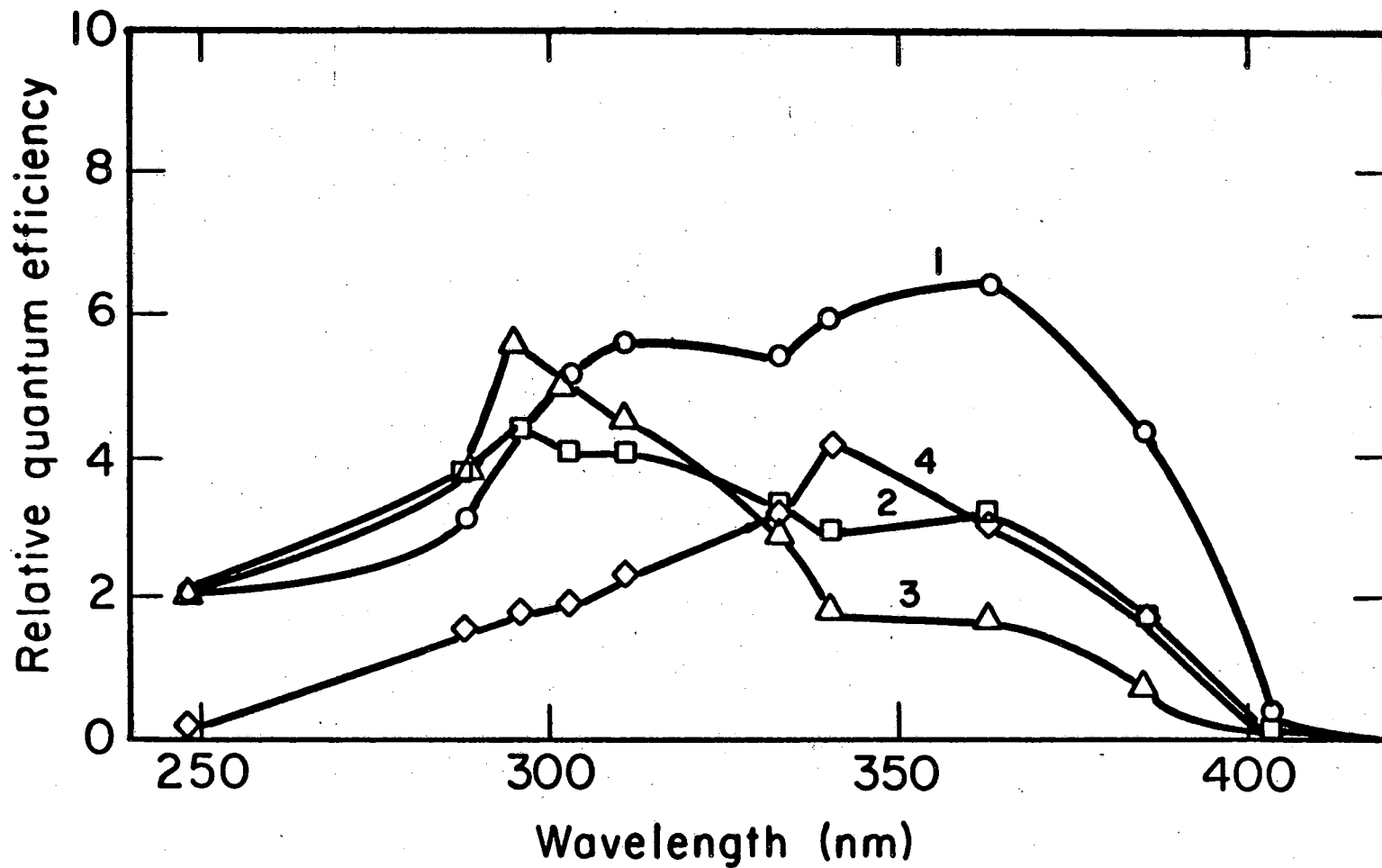
Differences in film structure are the most likely cause of the difference in photoelectrochemical properties. The results from Section 3.3.4.1 indicate that the crystalline grain size decreases with increasing rf power. A reduction in crystallite size causes higher recombination rates and therefore lower photocurrents (109-111).

Photoresponse - wavelength properties for the anodes described in Figure 48 are shown in Figure 49. The long



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Fig. 48. Effect of rf power on photocurrent density: 1. 10 watts, 2. 100 watts, 3. 200 watts.



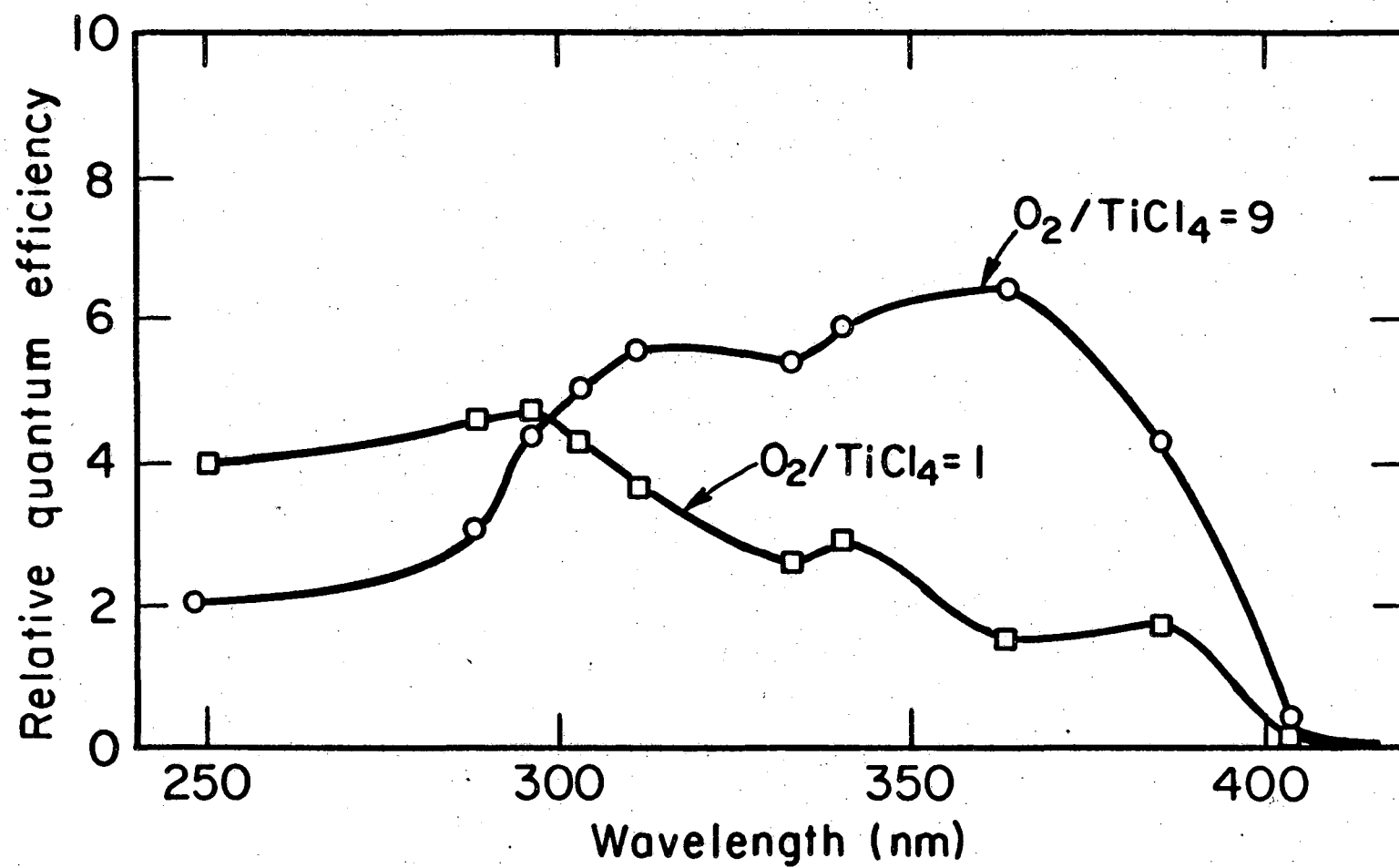
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Fig. 49. Effect of rf power on action spectra: 1. 10 watts, 2. 100 watts, 3. 200 watts, 4. thermally grown film (for comparison).

wavelength response for the 10 watt deposition, Curve 1, is a factor of three higher than that for the 100 and 200 watt depositions. However, the response for the three films at the shorter wavelengths (303 nm and lower) are nearly equal. Usually, photocurrents in the short wavelength region are controlled by surface recombination (15,51) while the photocurrents for the long wavelengths are controlled by bulk recombination (15). Apparently the poor response for the films deposited at 100 and 200 watts rf power for long wavelengths result from higher bulk recombination rates caused by the high density of grain boundary recombination sites. In view of these results, all the anodes for the remainder of this study were made at rf powers of 20 watts or less.

3.6.5 Comparison Between Thermally Grown Anodes And Improved Deposited Anodes

For comparison, the photoresponse for the thermally grown photoanode discussed earlier is also shown in Figure 49. This time, the titanium dioxide photoanode that was plasma deposited at 10 watts has a greater photoresponse than the thermally grown anode over the entire spectrum. Thus, the photoelectrochemical properties of the plasma deposited anode has been improved by increasing the feed gas ratio of oxygen to titanium tetrachloride. This is explicitly shown in Figure 50 by the photoresponse - wavelength curves for two films of equal thickness (1.15



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Fig. 50. Effect of reactant gas composition on photo-response.

microns) but deposited using two different oxygen to titanium tetrachloride ratios, 9 and 1 respectively.

By proper selection of the deposition conditions, plasma deposited photoanodes can be tailored to have photoelectrochemical properties that are much better than those for the thermally grown photoanodes. At least part of the difference in photoelectrochemical properties is related to differences in the structural properties of the thermally grown films compared to the plasma deposited films. In Section 3.3.5, Film Structure, it was shown that the plasma deposited films had larger and more uniformly oriented crystallites (columnar structure) than the thermally grown films. As a result, photogenerated charge carriers encounter fewer grain boundaries in the plasma deposited film than in the thermally grown film.

3.6.6 Effect Of Chlorine On Photoelectrochemical Properties

During the deposition process, the plasma deposited films are exposed to chlorine, and as shown in Section 3.5, Electronic Properties, the presence of chlorine in the film can affect the capacitance - voltage and current voltage characteristics of these films. It is possible that chlorine may alter some of the other electronic properties which help to determine the photoelectrochemical behavior.

There have been numerous reports of improving the electronic and photoelectronic properties of semiconductors by incorporating various elements. One of the most

extensively studied areas is the incorporation of hydrogen in amorphous silicon by glow discharge deposition from silane (71,112-114). The effect of the hydrogen is complex; the optical and electronic properties are both modified. For the electronic properties, the most important change is the reduction in the density of dangling bonds and defect states which leads to lower recombination rates (115-116). Other methods of incorporating hydrogen into silicon have also been reported. For example, Seager (115) introduced monatomic hydrogen into polycrystalline silicon by heating the silicon (400 C) in a hydrogen glow discharge. He found that the treatment passivated the grain boundaries and increased the solar energy conversion efficiency of the polysilicon.

Some semiconductors have also had improvements made in their electronic properties by treating them with fluorine. Stringfellow (117) etched gallium phosphide in a carbon tetrafluoride glow discharge and found fluorine adsorbed on the surface after etching. While fluorine was present, there was a reduction in the surface recombination rate and an increase in the minority carrier diffusion length. Cockrun et al. (118) ion implanted silicon wafers with fluorine; as a result, the minority carrier lifetime increased. The photoelectrochemical properties of titanium dioxide treated in fluorine have been reported by Subbarao et al. (57,119). They fluorinated single crystal rutile by heating the crystal (575 to 700 C) in a mixture of hydrogen

fluoride and argon. The fluorinated anodes were compared with untreated single crystal rutile photoanodes and were found to have higher quantum efficiencies, particularly at the longer wavelengths. The improvement in properties was attributed to a reduction in the recombination site density resulting from filling the oxygen vacancies with fluorine ions. In view of these results and considering the similarities between fluorine and chlorine, it is reasonable to expect that chlorine may affect the photoelectrochemical properties of the plasma deposited anodes used in the present study.

If the chlorine exposure received by the plasma deposited anodes enhances the photoelectrochemical properties, this will in part account for some of the differences in performance of the thermally grown versus the plasma deposited photoanodes. To test the effect of chlorine on the photoelectrochemical properties of the thermally grown films, two methods were used to incorporate chlorine into the photoanodes. In the first method, the titanium substrate was oxidized in a mixture of chlorine and oxygen (100 cc/min oxygen and 10 cc/min chlorine) at 700 C. The films obtained by this method were of poor quality; they consisted of large brown-yellow flakes of titanium dioxide which had separated from the titanium substrate. This method was therefore abandoned.

In the second method, thermally grown titanium dioxide films were annealed in a helium-chlorine mixture (10 to 1

ratio). Four titanium substrates were oxidized in oxygen for 30 minutes at 700 C. One of the thermally grown films was annealed in pure helium at 500 C for 12 minutes, and was then reduced in a helium - hydrogen mixture at 600 C for 30 minutes. The second film was annealed in the helium - chlorine mixture at 500 C for 12 minutes followed by the same helium - hydrogen reduction as the standard. The third film was also annealed in the helium - chlorine mixture for 12 minutes at 500 C, but the helium - hydrogen reduction was not performed. A temperature of 300 C was used for a helium - chlorine treatment of the fourth film and the helium - hydrogen reduction was not performed.

Figure 51 shows the photocurrent - voltage properties for the four films described above and also summarizes the experimental conditions. The standard film (no chlorine treatment), Curve 1, shows a much lower photoresponse than any of the photoanodes treated with chlorine, Curves 2-4. The photoanodes treated in chlorine at 500 C, Curves 2 and 3, display photocurrents that are more than a factor of two higher than that for the standard case. Also, notice that sample 2, which received the 500 C chlorine treatment and the reduction treatment, shows a slightly lower photocurrent than for sample 3, which only received the chlorine treatment at 500 C. This difference is probably a result of the difference in conductivities; the reduced film had a much higher dark current. The important point here is that hydrogen - helium treatment does not significantly affect

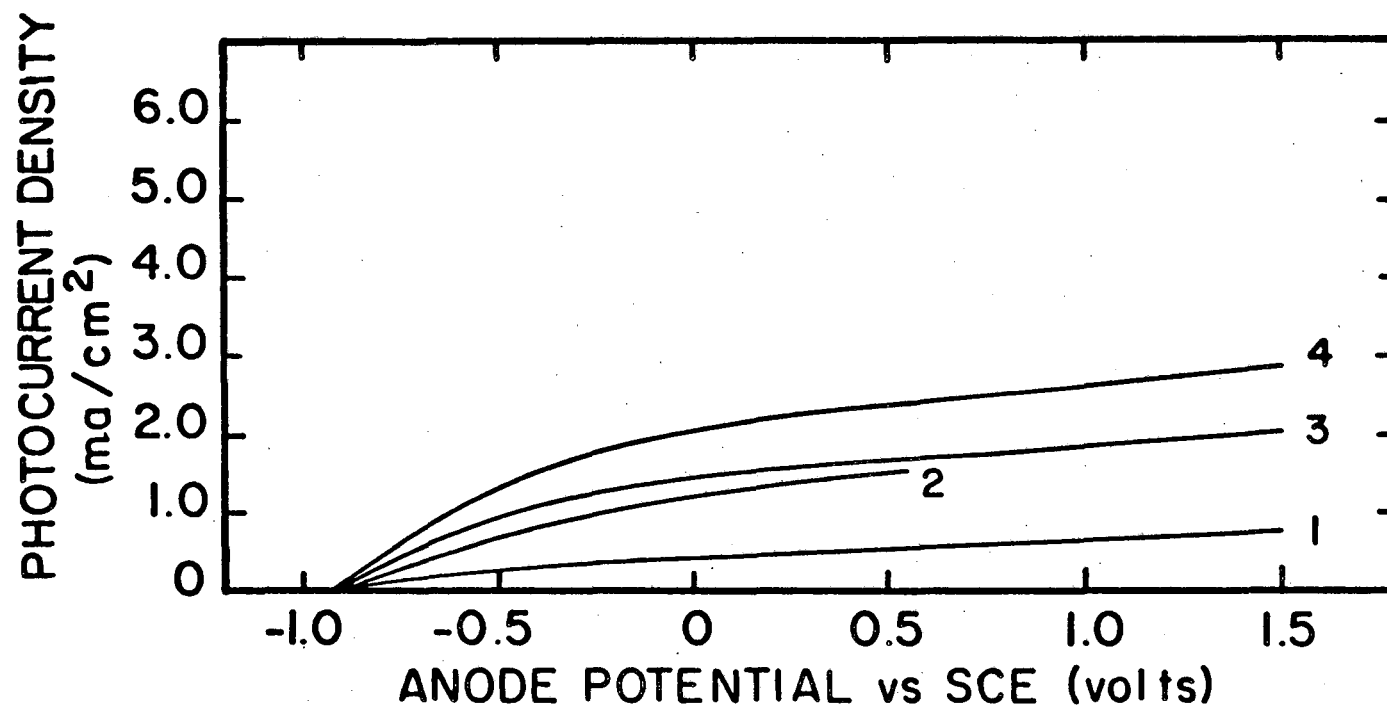


Fig. 51. Effect of chlorination on thermally grown photoanode performance. Anneal gas and temperature conditions: 1. helium at 500 C then hydrogen - helium at 600 C, 2. chlorine - helium at 500 C then hydrogen - helium at 600 C, 3. chlorine - helium at 500 C, 4. chlorine - helium at 300 C.

the saturation photocurrents. The fourth film, Curve 4, (chlorine treatment at 300 C) has a higher photocurrent than the other three anodes; it is three times higher than the unchlorinated anode. Apparently, the improvements induced by the chlorine seem to be more favored by the lower temperature treatment.

It is now apparent that annealing thermally grown films in a chlorine - helium mixture improves their photoelectrochemical properties. Thus, the chlorination seems to affect the thermally grown films in a way similar to that reported by Subbarao et al. (57,119) for the fluorination of single crystal titanium dioxide. Also of interest is the fact that the largest improvement in properties for the fluorination (57) and for the chlorination occurs at lower temperatures.

Further studies of the chlorination of thermally grown anodes were made in order to determine its effect on the photocurrent - wavelength properties and also to examine the chlorination time dependence of the property changes. In this series, three titanium substrates were oxidized (700 C, 30 min, in oxygen) and then reduced (600 C, 30 min, 10% hydrogen - 90% helium). Again, one of the thermally grown titanium dioxide films was used as a standard and was not chlorinated. The other two were chlorinated at 350 C in a 10 to 1 helium-chlorine mixture for 15 minutes and 30 minutes respectively. Photoanodes were then fabricated, and the current - wavelength properties were measured.

Figure 52 shows the results of the current - wavelength measurements as the photocurrent ratio vs wavelength. The photocurrent ratio is defined as the photocurrent for the anode divided by the photocurrent for the standard anode. Thus, the photocurrent ratio represents an improvement factor. The two sets of data shown in Figure 52 are for the two films chlorinated for 15 and 30 minutes respectively. Of course, the photocurrent ratio for the standard anode is equal to 1 over the entire spectrum. Both chlorination treatments yield significant improvements in the photoanode performance. Note that the photocurrent ratio for the 30 minute chlorination is about a factor of two higher than that for the 15 minute chlorination. It may be possible to improve the response further by chlorinating the oxide for longer periods of time.

The variation of photocurrent ratios with wavelength is particularly interesting. The chlorination yields little, if any, improvement in the photocurrent for light of wavelengths greater than about 380 nm. However, at shorter wavelengths (less than 370 nm) the photocurrent for the 15 minute chlorination is 8 to 10 times higher than that for the unchlorinated anode, while the 30 minute chlorination results in a factor of 15 to 20 increase in the photocurrent over that for the unchlorinated anode. This increase in the photoresponse for light at the short wavelength end of the spectrum implies that the surface recombination rate has been reduced (15). Thus it is believed that the

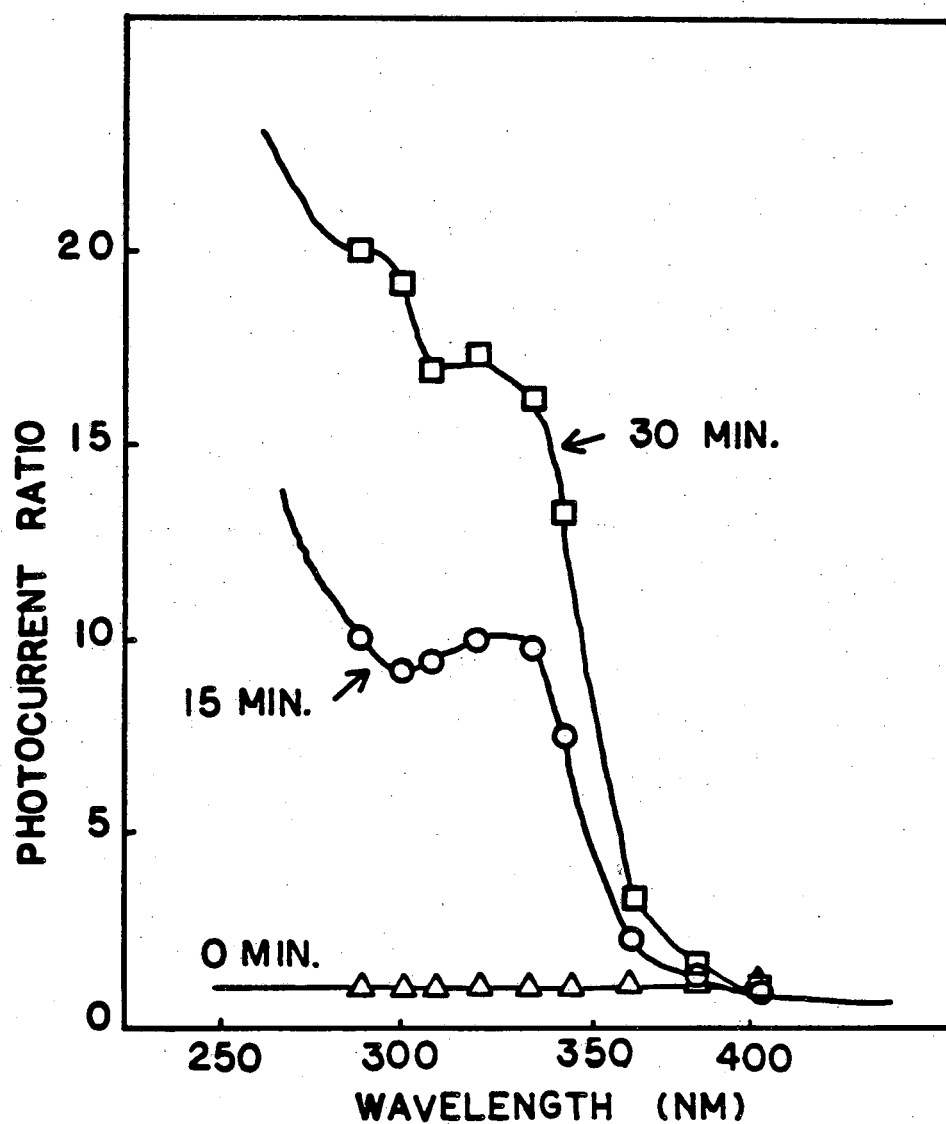


Fig. 52. Effect of chlorination on action spectra of thermally grown photoanodes. Photocurrent Ratio = photocurrent / photocurrent for unchlorinated anode. Chlorination at 350 C in chlorine - helium mixture for the times indicated.

chlorination leads to a reduction in surface recombination and/or grain boundary recombination sites. However, even with the observed improvement, the photoresponse is still much less than that for the best plasma deposited anodes.

As stated earlier, the plasma deposited photoanodes showed a higher short wavelength response than the thermally grown films i.e. lower surface recombination rate. To check for further possible improvements, several plasma deposited titanium dioxide films were given a post-deposition chlorination. Three plasma deposited films were given the same chlorination treatments described above for the three thermally grown films. Photocurrent - wavelength curves were measured for the films, and it was found that the chlorination treatment did not significantly change the photoelectrochemical properties. It should be noted that the plasma deposited anodes had much better photoelectrochemical properties than the thermally grown anodes and thus had less room for improvement.

3.6.6.1 Speculations On The Chemical Effect of Chlorine

It has been established that chlorination of the thermally grown films improves their short wavelength photoelectrochemical properties. It is also known, by nature of the reactant gas involved, that the plasma deposited titanium dioxide films are exposed to chlorine throughout the deposition process; this chlorine exposure may help to improve their photoelectrochemical properties.

Based on Auger and ESCA results (see Section 3.2) very little chlorine is present in the deposited films used as photoanodes. In addition, the structural properties (see Section 3.3.5) show that only the rutile phase is present in both the deposited photoanodes and the thermally grown anodes. Rutile has a relatively compact lattice and cannot easily accomodate chloride ion impurities. The chlorine -1 ion has a radius of 1.80 angstroms; the oxygen -2 ion has a radius of 1.40 angstroms; the titanium $+4$ ion has a radius of 0.64 angstroms (120). Thus the chlorine is too large to fit on a lattice site without inducing a large amount of lattice stress. Furthermore, the packing factor for rutile, 0.83, is rather high, and so the chlorine ion cannot occupy an interstitial site. However, the structure at grain boundaries is quite open, and the chlorine, if present, can be situated at the grain boundaries in a film. Grain boundaries are also a primary source of recombination sites in polycrystalline films (115,116). Therefore, if present at the grain boundaries, the chlorine could serve to reduce the recombination rate by direct interaction with the recombination sites.

There is also the possibility that chlorine incorporation is unnecessary for the improved photoresponse. In this senario, chlorine treatments or exposures serve to modify the titanium dioxide surface and/or grain boundaries such that the recomination rate is reduced but the chlorine would not remain in the film. This concept is supported by

the statement by Ghoshtagore (79) that chlorine is not known to be strongly adsorbed on rutile. It is also supported by the observation described earlier (see Figure 51) for the thermally grown anode that was reduced (600 C, hydrogen - helium mixture) after the chlorination treatment. The reduction should have removed most of the chlorine, if present, yet the anode still had a much better photoresponse than the unchlorinated anode.

The mechanism behind the changes produced by the chlorine exposure is still unresolved. However, the important fact is that the chlorine seems to have a beneficial influence on the short wavelength photoelectrochemical properties of the anodes. This may be part of the reason why the plasma deposited anodes perform better than the thermally grown anodes.

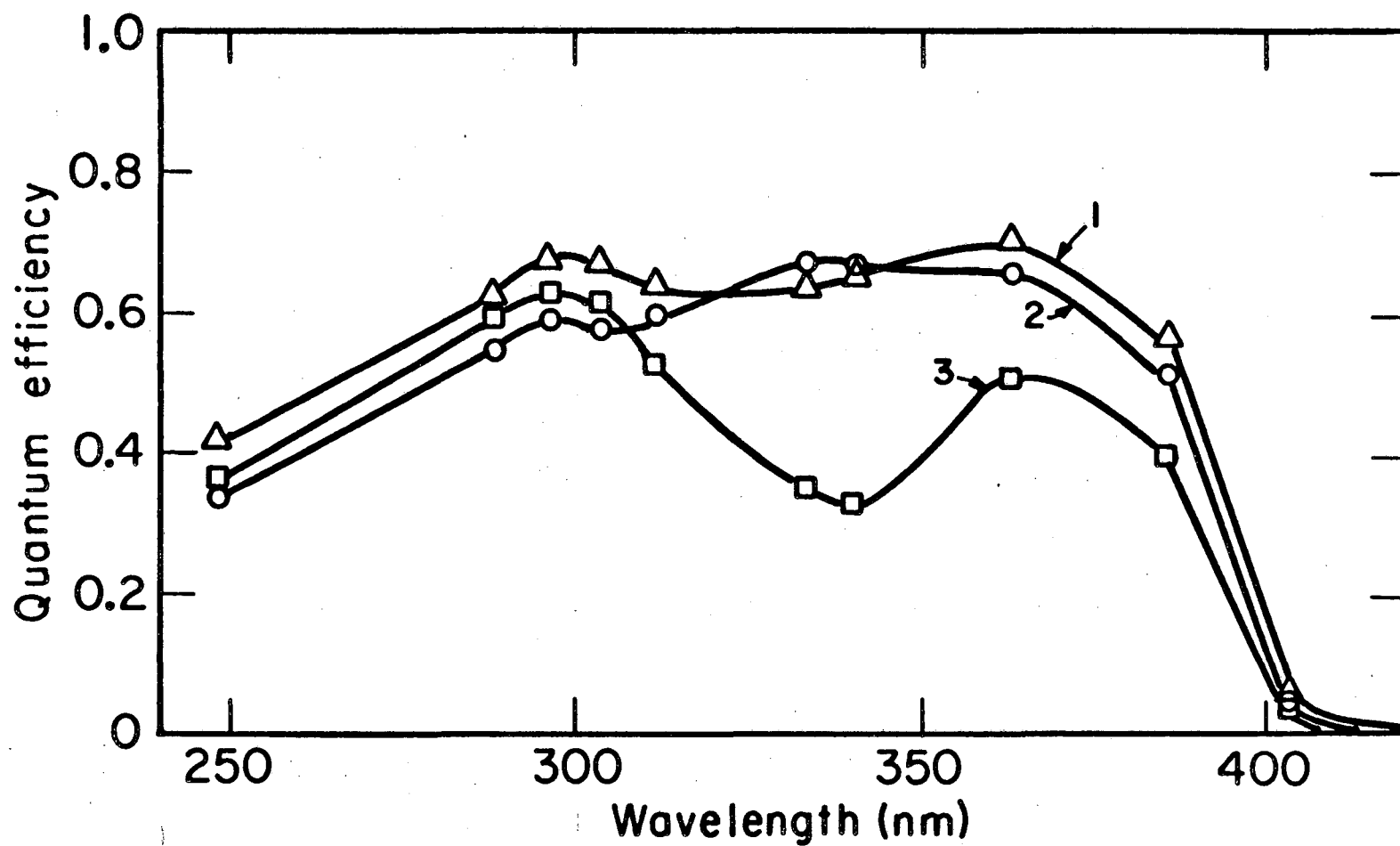
3.6.7 Differences In Long Wavelength Response

Thin film photoresponse for long wavelength radiation is largely determined by the thickness of the film. The absorption coefficient (see Section 3.4) is lower for the long wavelengths and so the film must be thicker to allow absorption of the longer wavelengths than is needed for absorbing the shorter wavelengths. The best plasma deposited titanium dioxide photanodes are thicker than the best thermally grown photoanodes and, as expected on the basis of light absorption, the long wavelength response is greater than that for the thermally grown anodes. As

mentioned earlier, thick film (greater than 0.8 microns) thermally grown oxides did not work as well as the thin oxides. This may only be a problem of further optimizing the oxidation conditions. But it may also be related to the bulk recombination rates; the thermally grown films have smaller grains (see Section 3.3.5) and thus higher recombination rates (116). The deposited anodes have larger, better-oriented crystallites and thus a lower recombination rate. As a result of the lower bulk recombination rate, the plasma deposited anodes can have a greater thickness than the thermal oxides without a loss in performance. This explanation agrees with the photoresponse results that Kumari (121) reports for polycrystalline silicon. He shows that by increasing the grain size, the photoresponse for the long wavelength light shows significant increases while the short wavelength response shows much smaller changes.

3.6.8 Additional Results For Plasma Deposited Photoanodes

Quantum efficiencies for several of the plasma deposited titanium dioxide photoanodes were measured for comparison with the results reported by other investigators. Figure 53 shows the quantum efficiency as a function of wavelength for films deposited using the following conditions: 40 micromoles per minute of titanium tetrachloride, 360 micromoles per minute of oxygen, temperature of 600 C. Curves 1 and 3, for anodes deposited



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Fig. 53. Action spectra for plasma deposited photoanodes: 1. 1.2 microns thick, 10 watts rf power; 2. 1.3 microns thick, 10 watts rf power; 3. 1.5 microns thick, 5 watts rf power.

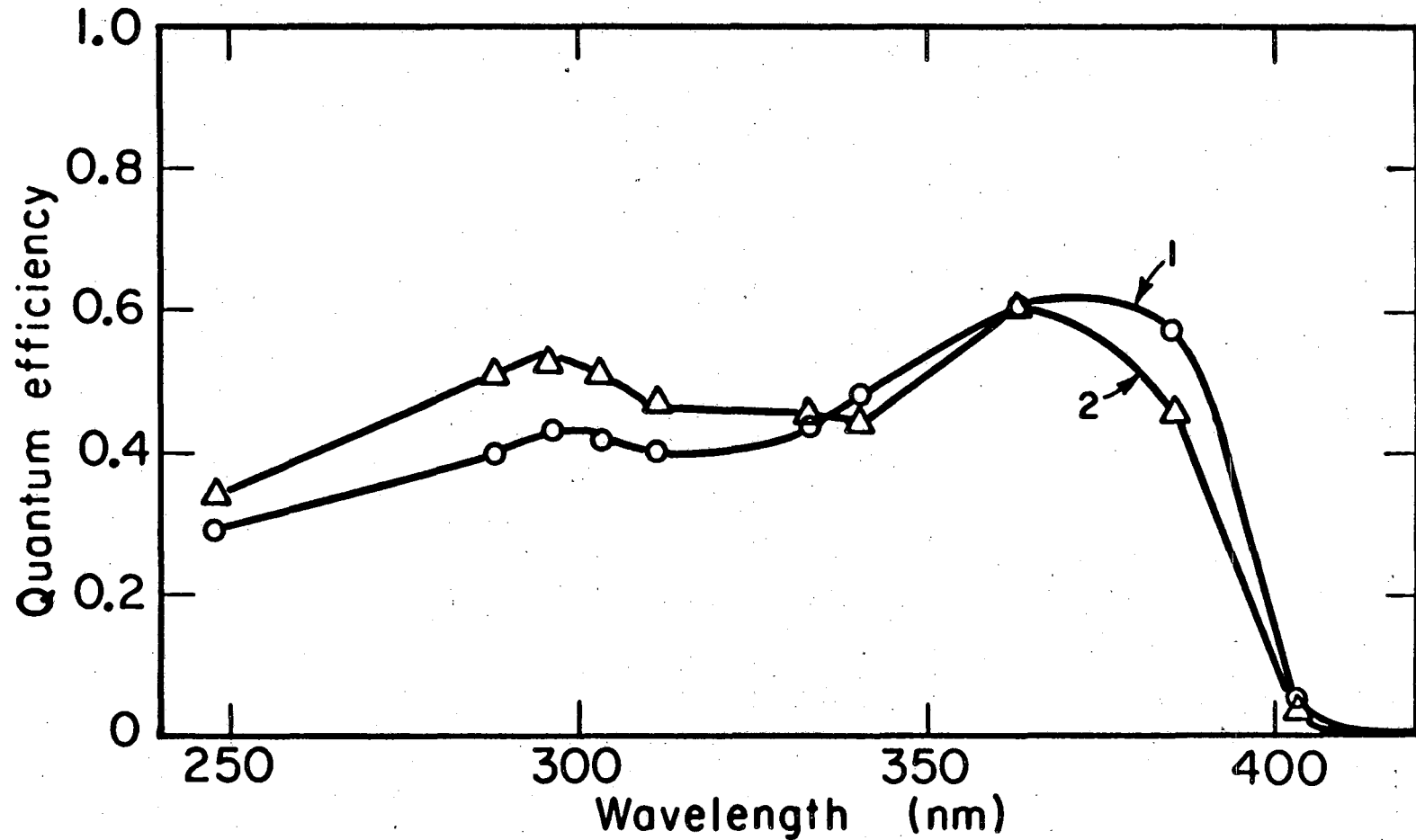
using an rf power of 10 watts, have thicknesses of 1.2 microns and 1.3 microns respectively while Curve 2, for an anode deposited at 5 watts rf power, has a thickness of 1.5 microns. The quantum efficiencies shown by Curves 1 and 2 are similar in magnitude to those reported by Wilson et al. (22) and Harris et al. (23) for single crystal rutile photanodes (1 mm thick). Their experimental conditions were different from those of the present study; they used 1 molar potassium hydroxide for the electrolyte and an anode potential of 0.0 volts vs SCE instead of 1 molar sodium hydroxide and +0.125 volts. They subjected their photanodes to a variety of surface treatments and were able to obtain quantum efficiencies that were usually in the 0.5 to 0.75 range. Curves 1 and 2 show quantum efficiencies of 0.6 to 0.7 over the wavelength range of 290 to 365 nm. It is particularly interesting that such high quantum efficiencies are obtained for the longer wavelengths (363 nm) in view of the fact that the films are too thin for complete absorption of incident light. This behavior suggests that the actual recombination rate in the plasma deposited anodes, for the longer wavelengths, is very low and the quantum efficiency, if corrected for actual light absorption, is nearly 100%. The drop in quantum efficiency at short wavelengths (250 to 290 nm) is caused by surface recombination as well as losses due to absorption by the electrolyte.

There is a slight dip in the quantum efficiency for Curves 1 and 2 between the wavelengths of 303 nm and 363 nm.

Some of the plasma deposited anodes, such as the one described by Curve 3, have a much greater dip in the quantum efficiency. The cause of the dip in the quantum efficiency is unclear. Reflectance measurements (see Section 3.4) show only a small (less than 3%), smooth increase for that wavelength range. Light transmittance measurements (see Section 3.4) show no changes that would cause a dip in the quantum efficiency. Thus, the dip is not believed to be related to the optical properties. The thermally grown anodes made in this study cannot have such a dip in quantum efficiency because the photoresponse for the long wavelength light (near bandgap) and at the shorter wavelengths (311 nm and less) are both fairly low and so a peak in the 330 to 340 nm range is generally observed (see Figure 49). Other investigators (22,90) also show dips in their wavelength response measurements.

Polished titanium substrates (mirror finish with 1 micron diamond paste) were also used to fabricate plasma deposited photoanodes. The purpose of using the polished substrates was to compare them with the rough, HF etched, substrates. After the photoelectrochemical measurements, aluminum dots were evaporated onto the plasma deposited titanium dioxide and used as electrical contacts for measuring the resistance and capacitance of the oxide (see Section 3.5, Electronic Properties).

Figure 54 illustrates the quantum efficiency - wavelength characteristics for two of the titanium dioxide

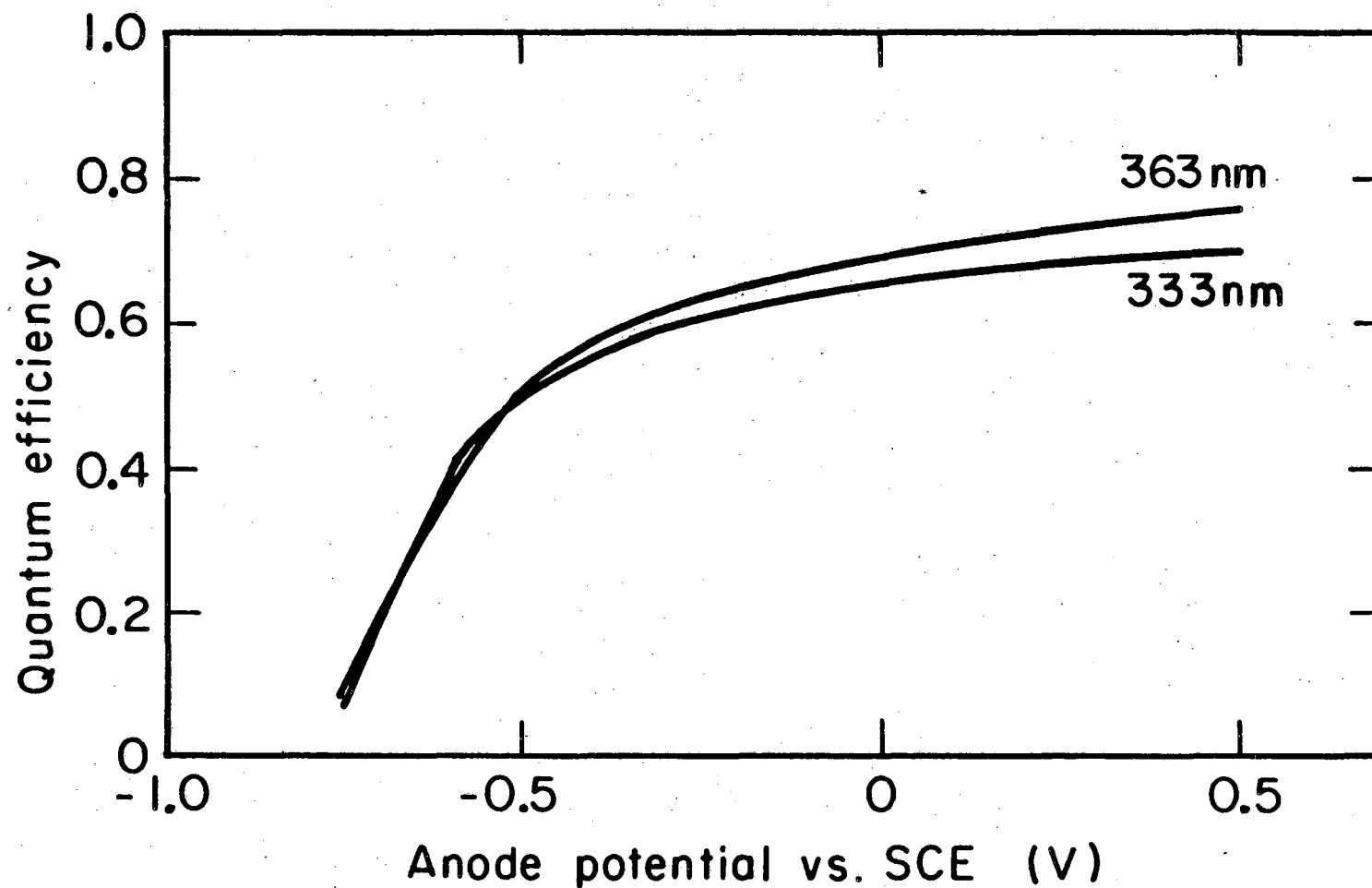


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Fig. 54. Action spectra for plasma deposited photoanodes on polished substrates: 1. resistivity 0.9 megohm-cm, 1.5 microns thick; 2. resistivity 0.6 megohm-cm, 1.3 microns thick.

films deposited onto polished titanium substrates. Curves 1 and 2 are for anodes made under the same conditions described earlier and at 5 watts and 20 watts rf power respectively. As expected, the photoresponse properties for these two films are similar to those for the films deposited onto the unpolished substrates. The film for Curve 1 is 1.5 microns thick, has a resistivity of 0.9 megohm-cm, and a dielectric constant of 166. By comparison, the film for Curve 2 is 1.3 microns thick, has a resistivity of 0.6 megohm-cm, and a dielectric constant of 157.

Quantum efficiency - voltage characteristics were also examined for the photoanodes using monochromatic light. Figure 55 shows the quantum efficiency - voltage characteristics for a photoanode deposited at 10 watts rf power. At low potentials (less than -0.5 volts), the quantum efficiency for the 363 nm light is approximately equal to that for the 333 nm light. The differences in the curves increase as the potential increases and at 0.5 volts the quantum efficiencies are 0.75 (363 nm light) and 0.70 (333 nm light). Wilson et al. (22) also reported quantum efficiency - wavelength data for his single crystal rutile using 350 nm light. A comparison between Wilson's results and the results for the plasma deposited photoanodes shows that the initial slope of the quantum efficiency - voltage curve is usually lower for the plasma deposited photoanodes than for the single crystal anodes. As a result, a higher potential is required for the plasma deposited anodes before



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Fig. 55. QE - Voltage data for titanium dioxide deposited on rough substrate at 10 watts rf power.

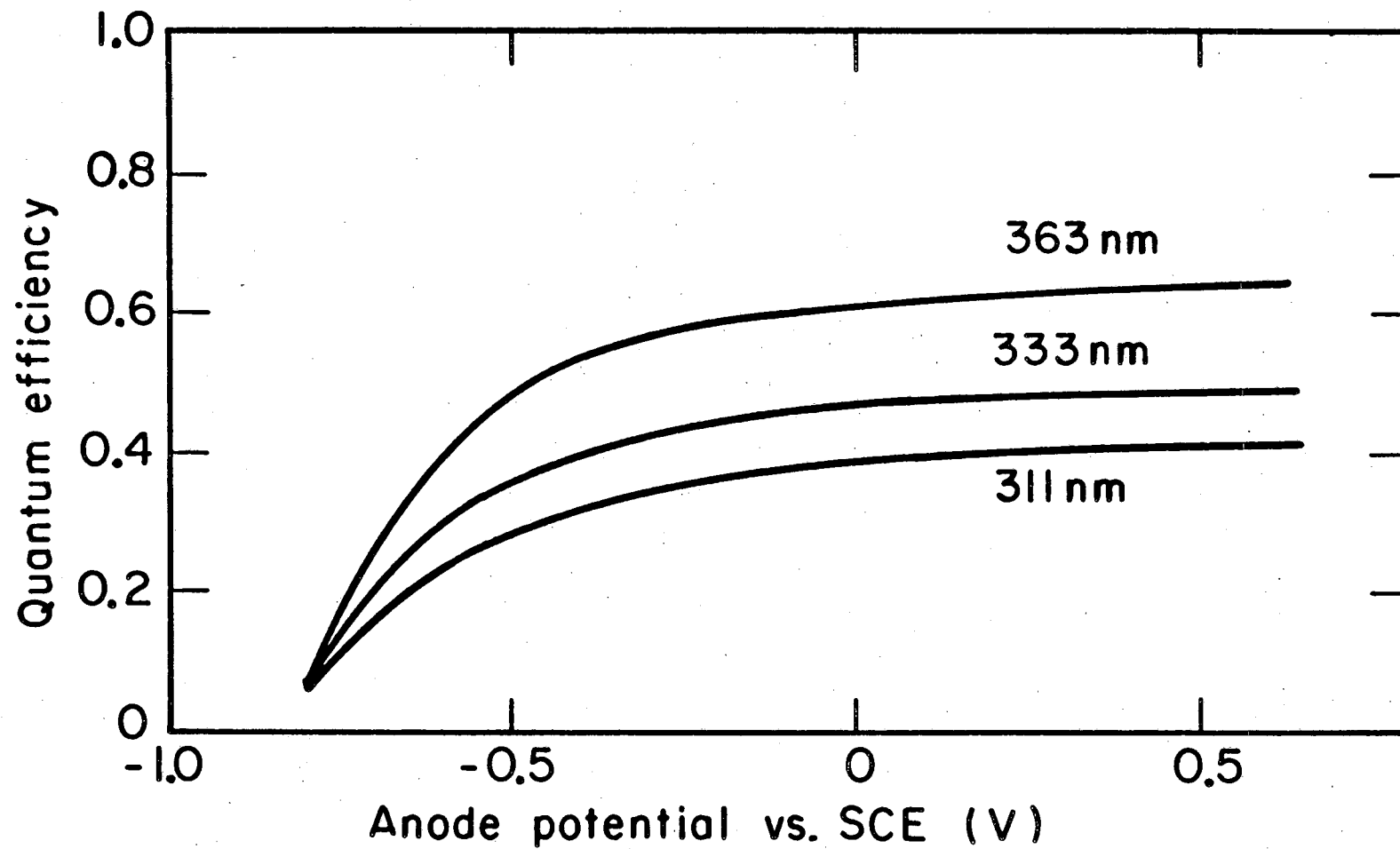
the maximum quantum efficiency is reached than for the single crystal anode. This is true even though the maximum quantum efficiency may be higher for the plasma deposited photoanode.

Quantum efficiency - voltage results for the two films deposited onto the polished titanium substrates discussed above are given in Figures 56 and 57. Their properties are similar to those for the unpolished photoanodes. Therefore, it seems that surface roughness is not an important factor for the anodes made in the present study.

3.6.9 Thickness Effects

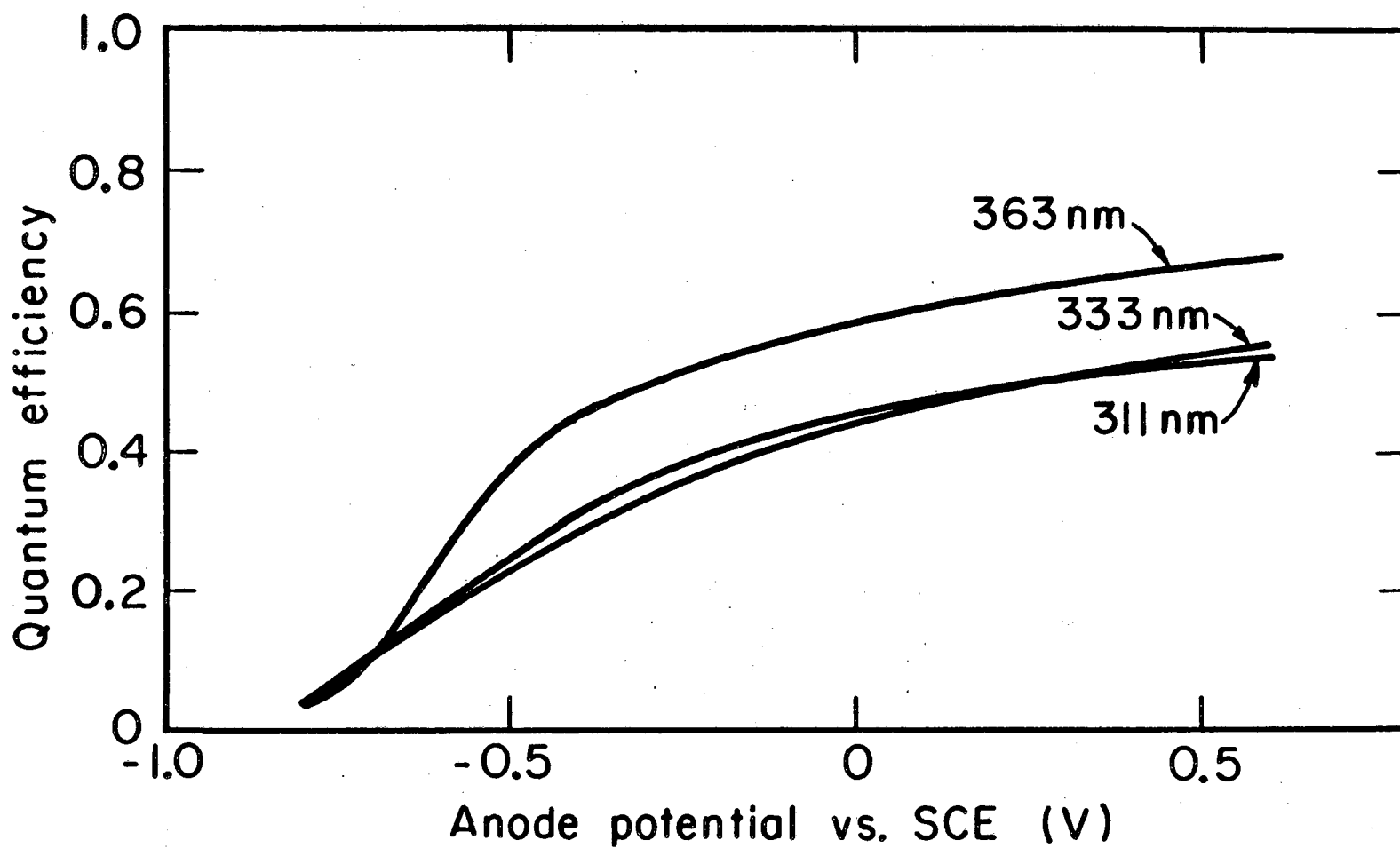
An optimum thickness exists for photoanodes. This optimum is determined by the optical and electronic properties of the material. A film that is too thin can not absorb all of the incident light while a film that is too thick imposes unnecessary ohmic losses and additional trapping and/or recombination problems.

For the purpose of further examining the film thickness dependence of the photoresponse for the plasma deposited photoanodes, three photoanodes were deposited under identical parameter settings but for differing lengths of time. The films that were obtained had thickness of 1.0 microns, 2.2 microns, and 4.0 microns. Quantum efficiency - wavelength curves for the three films are shown in Figure 58. The 2.2 micron film has better photoelectrochemical properties than the 1.0 micron film and the 4.0 micron film



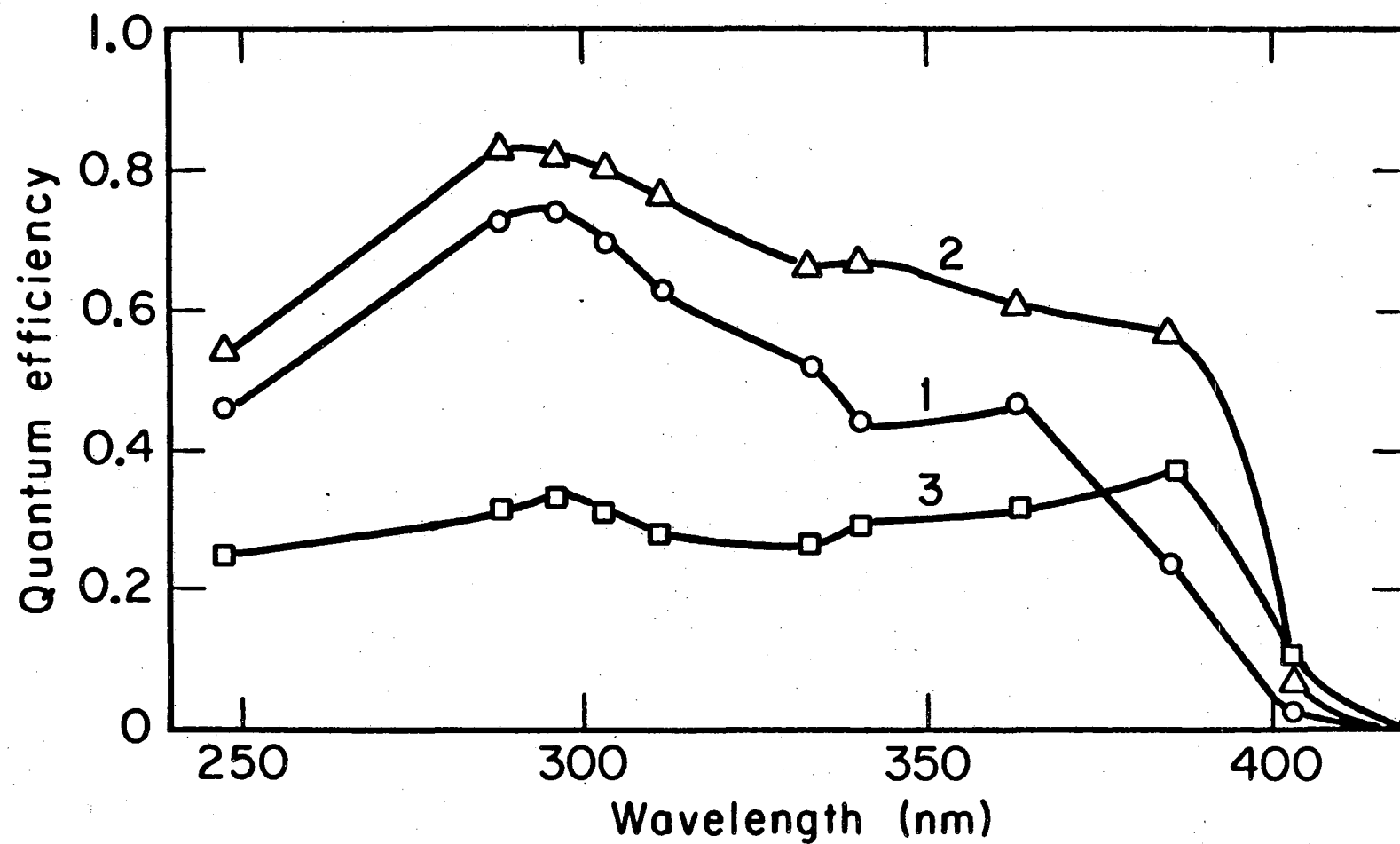
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Fig. 56. QE - Voltage data for titanium dioxide deposited on polished substrate at 5 watts rf power.



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Fig. 57. QE - Voltage data for titanium dioxide deposited on polished substrate at 20 watts rf power.



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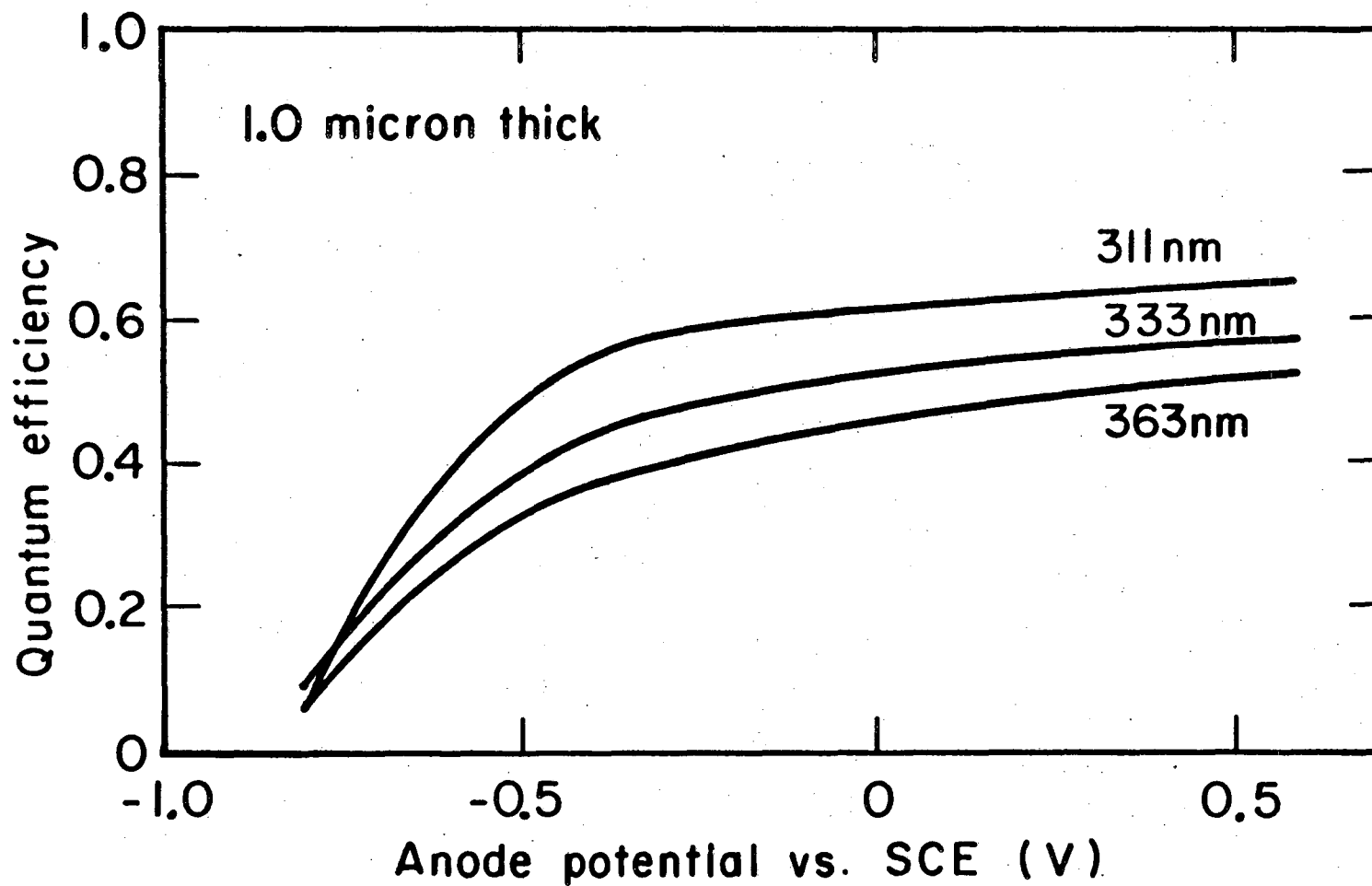
Fig. 58. Effect of film thickness on action spectra: 1. 1.0 microns thick, 2. 2.2 microns thick, 3. 4.0 microns thick.

over the entire spectrum. At wavelengths less than about 385 nm, the 1.0 micron film has much higher quantum efficiencies than the 4.0 micron film. Thus, these anodes show the expected behavior.

Additional differences between the 4.0 micron film and the other two films are illustrated by the quantum efficiency - voltage properties. Figures 59 and 60 show the properties for the 1.0 and 2.2 micron films; the properties are very similar for the films in terms of the shape of the curves and current onset; there are, as stated before, differences in the peak magnitudes. In contrast, the curves for the 4.0 micron film, Figure 61, have a different shape and require much higher potentials before the quantum efficiency begins to increase. In view of these results, it seems that the optimum thickness is approximately 2.0 microns for those deposition conditions.

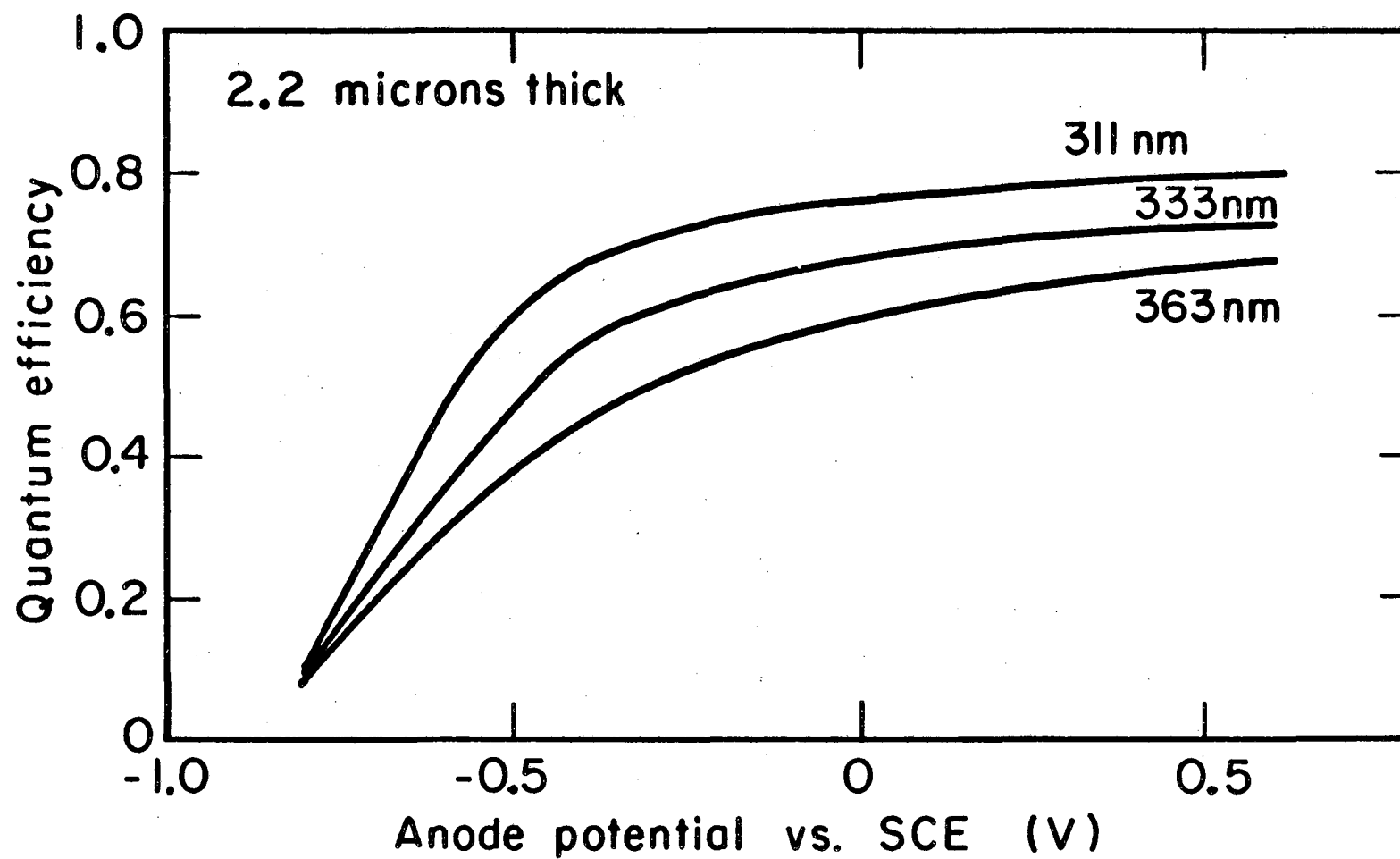
3.6.10 Photoanode Parameter Estimation

The Gartner model (122) of depletion layer photoeffects in semiconductors has been used by several investigators to calculate the carrier concentration for photoelectrodes (123-126). This model predicts the total photocurrent as a sum of the current for carriers generated within the depletion region and the current due to carriers generated in the adjacent bulk material which diffuse into the depletion region. In formulating the model, surface recombination and depletion layer recombination are



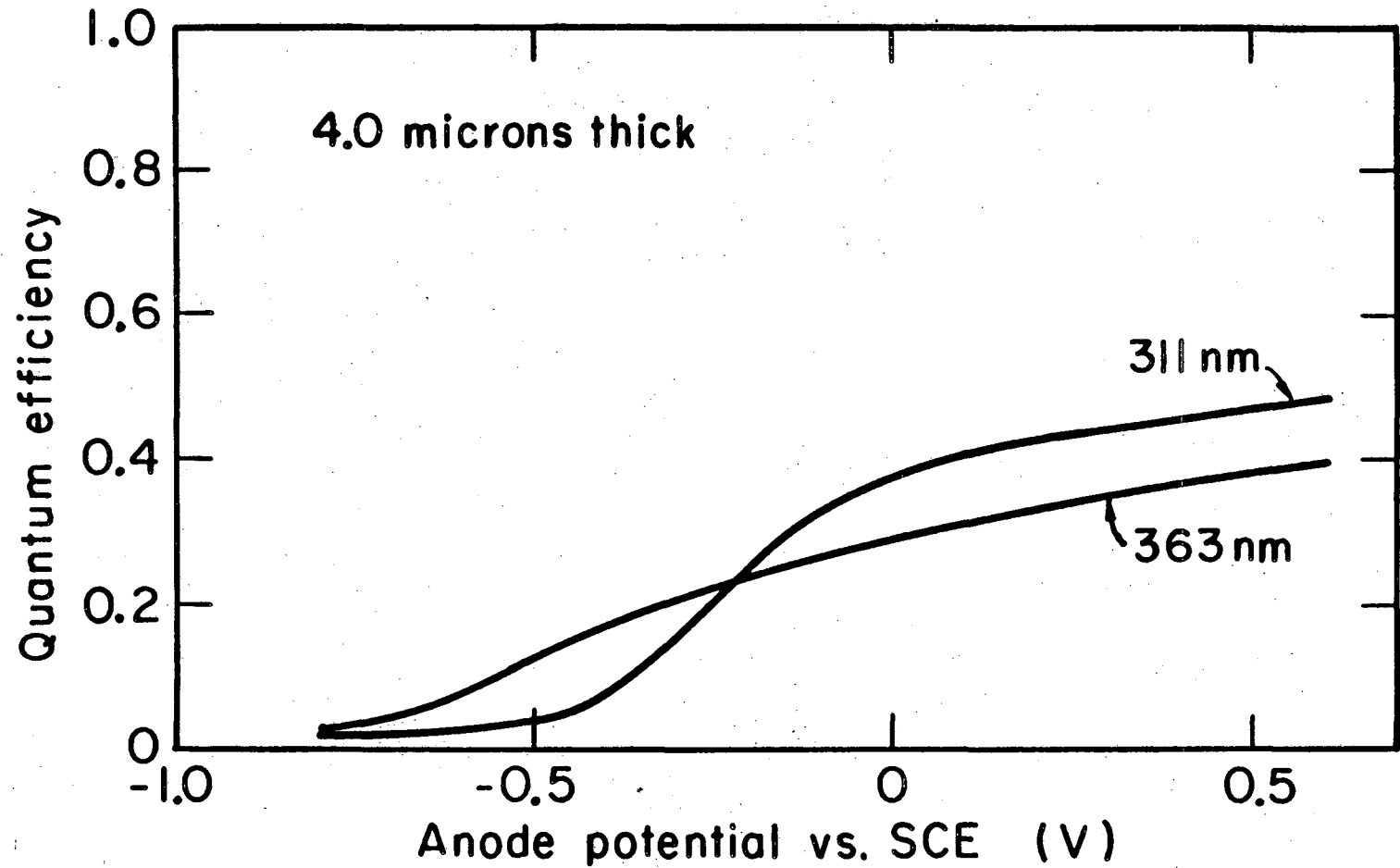
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Fig. 59. QE - Voltage data for 1.0 micron thick film.



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Fig. 60. QE - Voltage data for 2.2 micron thick film.



XBL828-4022

Fig. 61. QE - Voltage data for 4.0 micron thick film.

neglected. In addition, no corrections are made for the effect of the photogenerated carriers on the bending of the energy bands and on the depletion layer thickness.

When simplified for application to the semiconductor - electrolyte junction, the equation for the Gartner model used by Kennedy et al. (125) is

$$\eta = 1 - \exp(-\alpha W) (1 + \alpha L)^{-1} \quad (9.)$$

where η is the quantum efficiency, α is the absorption coefficient, W is the depletion layer width, and L is the minority carrier diffusion length in the bulk of the semiconductor. By definition, the minority carrier diffusion length is

$$L = (D\tau)^{0.5} \quad (10.)$$

where D and τ are the minority carrier diffusion coefficient and life time, respectively. Thus, L is partially determined by the bulk recombination rate. The depletion layer width is given by

$$W = (2k\epsilon/(eN))^{0.5} (V - V_{fb})^{0.5} \quad (11.)$$

where k is the dielectric constant, ϵ is the vacuum permittivity, e is the electron charge, N is the majority carrier density, V is the electrode potential, and V_{fb} is

the flatband potential. Substituting Equation 11 into Equation 9 and taking the natural logarithm yields

$$\ln(1 - \eta) = -\alpha(2k\epsilon/(eN))^{0.5}(V - V_{fb})^{0.5} - \ln(1 + \alpha L) \quad (12.)$$

A plot of $\ln(1 - \eta)$ as a function of $(V - V_{fb})$ gives a straight line with

$$\text{slope} = -\alpha(2k\epsilon/(eN))^{0.5} \quad (13.)$$

$$\text{intercept} = -\ln(1 + \alpha L) \quad (14.)$$

Thus, using the equations given above along with quantum efficiency - voltage data, dielectric constant, absorption coefficient, and flatband potential, values of the carrier density (electrons for n-type semiconductors) and the minority carrier (hole) diffusion length can be estimated.

Kennedy et al. (124) estimated carrier densities of barium titanate pressed - pellet photoanodes and also calculated the carrier densities using capacitance techniques and Mott-Schottky plots. The carrier densities predicted by the model were higher than those given by the Mott-Schottky calculations, but were of the same order of magnitude.

A computer program was written to fit the experimental

data for the present study to the linearized Gartner model, Equation 12. The calculated slopes and intercepts were used to estimate the electron concentration and the hole diffusion length for the plasma deposited titanium dioxide photoanodes. A listing of the program is presented in the Appendix. The input data for the calculations were (1) absorption coefficient calculated from the transmittance measurements (Section 3.4), (2) dielectric constant calculated from the capacitance measurements (Section 3.5.2), (3) the flatband voltage based on photocurrent onset, (4) and quantum efficiency - voltage data.

Typical outputs from the program are shown in the Appendix. The data used for two of those examples were from the quantum efficiency - voltage curves for the 333 nm light shown in Figures 55 and 56. Using the data in Figure 55, a carrier density of 1.3×10^{23} per cubic centimeter and a hole diffusion length of 37 nm were found. The data from Figure 56 gave similar results of 1.1×10^{24} per cubic centimeter and a hole diffusion length of 35 nm. By comparison, single crystal rutile has a hole diffusion length of 1000 nm (127). Thus, the diffusion lengths obtained from the model for plasma deposited photoanodes "seem" reasonable for polycrystalline films. However, the predicted carrier densities for the films are large when compared to the resistivities of the films.

For n-type semiconductors, the carrier density and resistivity are related by the equation

$$\text{resistivity} = (\mu N e)^{-1} \quad (15.)$$

where μ is the electron mobility, N is the carrier (electron) density, and e is the electron charge (97). From the modeling calculations, a typical carrier density is 1.0×10^{23} per cubic centimeter. Based on the electronic measurements from Section 3.5.2, a typical resistivity for the photoanodes is 1.0×10^6 ohm-cm. Using those values, Equation 15 gives an electron mobility of approximately 1.0×10^{-10} sq cm / volt-sec. This value is nine orders of magnitude lower than the value measured for polycrystalline rutile (24). Apparently, the Gartner model over predicts the carrier concentration and does not apply to the plasma deposited photoanodes.

If it is assumed that the electron mobility for the plasma deposited titanium dioxide approximately equals that for bulk polycrystalline rutile, then a value of the carrier concentration can be estimated. Using Equation 15, a resistivity of 1.0×10^6 ohm-cm, and a mobility of 0.1 sq cm / volt-sec, the calculated carrier density is approximately 1.0×10^{14} per cubic centimeter. Thus, the photoanodes fabricated in the present study probably have a low carrier density compared to that usually used for rutile photoanodes (1.0×10^{17} to 1.0×10^{20}) (22). As a result of the low carrier concentration, these plasma deposited photoanodes should have a large depletion region. Thus, a large fraction of

the incident light is absorbed within the depletion region, and high quantum efficiencies are obtained -- even for the longer wavelengths (360 nm and above).

There are several possible explanations why the Gartner model does not apply to the photoanodes fabricated in the present study. According to Wilson et al. (127), the assumption that the photogenerated charge carriers do not significantly alter the bending of the energy bands in the depletion region is valid for current densities of 1 microamp per square centimeter if the carrier density is at least 1.0×10^{16} per cubic centimeter. In the present study, the current densities were approximately 5 microamps per square centimeter and the carrier densities, as stated above, are probably less than 1.0×10^{16} per cubic centimeter; therefore, one of the requirements of the model is not met. In addition, as a result of the low carrier density, the depletion region is very large. Using Equation 11, $k=160$, and $N=1.0 \times 10^{16}$, the calculated depletion layer thickness is greater than the film thickness. Consequently, the recombinations that occur for these films are either within the depletion region or at the surface; both of those processes are neglected in the Gartner model.

Clearly, a model that is more complex than the Gartner model is required to describe the photoanodes fabricated in the present study. Models that account for surface and depletion region recombinations and light intensity effects have been developed by other investigators (127-130).

However, those models require additional parameters (mainly recombination rate data) which are usually unavailable. Thus, without additional data, these models would be of limited use in analyzing the photoanodes fabricated in the present study.

4.0 CONCLUSIONS

1. DEPOSITION RATE

Thin films of titanium dioxide can be deposited at temperatures ranging from near ambient to 700 C using a glow discharge to enhance the reaction rate between titanium tetrachloride and oxygen. The deposition rate depends on the deposition conditions, and rates as high as 0.3 microns per minute can be obtained. The activation energy for the plasma enhanced reaction is 0.12 eV/atom.

2. COMPOSITION

SIMS and AES show that chlorine is present in the films deposited at low temperatures (200 C and below). Chlorine is undetectable in films deposited at or above 400 C and in any film that received a 600 C anneal in oxygen. AES shows peak-to-peak oxygen to titanium ratios ranging from 1.24 to 1.47.

3. FILM STRUCTURE

Depositing the films onto glass substrates yields amorphous films (i.e. no x-ray diffraction peaks) for temperatures less than 300 C, anatase at 300 and 400 C, a mixture of anatase and rutile at 500 C, and only rutile at 600 C and above. This same progression in structures occurs for sodium chloride, silicon, sapphire, and titanium substrates, but the temperatures differ for each substrate.

Generally, all of the crystalline films show some preferred orientation.

Transmission electron diffraction patterns and micrographs of films deposited onto sodium chloride at 300 C suggest that the films are amorphous and agree with the x-ray diffraction results. Electron diffraction patterns of the films deposited onto sodium chloride at 700 C show a high degree of preferred orientation.

For the temperature range examined in the present study, the titanium dioxide films deposited onto sapphire substrates have the largest crystallites (some as much as 5 microns long). These are anatase films and are obtained at 400 C. In general, larger crystallites are obtained at low rf power (10 watts or less) than at high rf power (100 watts or greater).

Titanium dioxide films deposited onto titanium substrates show the presence of rutile at a lower temperature than that for the other substrates. Films plasma deposited onto titanium at 600 C have larger, better - oriented (columnar growth) crystallites than the films thermally grown on titanium at 700 C.

Selectivity between anatase, rutile or a mixture of the two occurs in the films is believed to be related to the energy and energy distribution of the nucleation sites. The energy of the sites is believed to be a characteristic of the substrate material and the temperature.

The plasma deposited titanium dioxide films have

crystallites that are larger than those obtained at comparable temperatures by CVD. This behavior suggests that the plasma may also enhance the crystallite growth. Considering the large grain size and high degree of preferred orientation, it may be possible to obtain plasma deposited epitaxial titanium dioxide films at lower temperatures than is required for other deposition techniques.

4. OPTICAL PROPERTIES

Optical properties for the plasma deposited titanium dioxide films are analogous to those for titanium dioxide films made by other methods.

5. ELECTRONIC PROPERTIES

Dielectric constants for titanium dioxide films deposited at 200 - 250 C are between 25 and 30 while the 600 C deposits have values of approximately 160. The presence of chlorine in the amorphous films alters the capacitance - voltage and current - voltage properties of the films. The chlorine acts as an electron acceptor; thus, the carrier concentration is reduced, and the films have better dielectric properties than the films containing little or no chlorine.

6. PHOTOELECTROCHEMICAL PROPERTIES

Plasma deposited titanium dioxide photoanodes can be

fabricated which have quantum efficiencies (60-80 %) comparable to those reported for single crystal rutile. The deposited anodes have higher quantum efficiencies than the thermally grown titanium dioxide anodes prepared in the present study. The difference in long wavelength photoresponse for the deposited films and the thermally grown films occurs as a result of the larger, better - oriented grain structure of the deposited films (i.e. fewer recombination sites). The chlorine exposure of the deposited films during the deposition may also contribute to the superior photoresponse of the deposited anodes -- particularly for the shorter wavelengths (less than 350 nm). This is supported by the observed increase in photoresponse of thermally grown anodes after being annealed in a chlorine - helium mixture. The improvement in photocurrent is most significant for wavelengths less than about 350 nm. Apparently, the chlorine exposure reduces the surface and/or grain boundary recombination site densities.

There is an optimum thickness for the photoelectrochemical properties of the plasma deposited photoanodes which depends on the deposition conditions. The optimum thickness was 1.5 to 2.0 microns for films deposited at 600 C, 10 watts rf power, and an oxygen to titanium tetrachloride ratio of 9.

Based on resistivity measurements, the anodes prepared in the present study have low carrier densities (less than 1.0×10^{16} per cubic centimeter). This low carrier density is

probably an important factor in making these photoanodes unsuitable for analysis using the Gartner model.

5.0 FUTURE WORK

5.1 Plasma Enhanced Deposition And Photoelectrochemistry

The most important advantage of plasma enhanced deposition for making photoanodes is the possibility of synthesizing new materials with the necessary optical, electronic, and chemical properties for efficient photoelectrolysis. As mentioned earlier, there have been efforts to extend the wavelength sensitivity of titanium dioxide (50,52-54,58,59) by incorporating additional elements that could, hopefully, reduce the effective bandgap. Except for fluorine addition, all of the elements added were cations. The cation is largely responsible for the energy level of the conduction band; for titanium dioxide the conduction band is determined by the titanium 3d band (24). Efforts to introduce another d-band level by adding other cations has resulted in minimal improvement in the photoresponse (52,55,58).

It may be possible to increase the wavelength response of titanium dioxide by changing the energy at which the valence band edge is located. The valence band for titanium dioxide is determined by the oxygen 2p energy level (24). By adding elements to the titanium oxide that are anions, it may be possible to reduce the effective bandgap. Some elements that may serve this purpose are nitrogen, sulfur, selenium, tellurium, and phosphorous. The ionic radii for those elements are larger than that for the oxygen -2 ion. New compounds made by these elemental additions would

necessarily have structural properties that are different from those for pure titanium dioxide. The possibility that these elements can lower the bandgap of the resulting oxide is further supported by the fact that the titanium nitrides, sulfides, and tellurides have bandgaps that are smaller than that for pure titanium dioxide (136). Some prospective reactions for synthesizing new titanium compounds are listed in Table 8. It should be possible to carry-out all of these reactions using a glow discharge with greater ease and versatility than can be achieved by other deposition methods.

5.2 Plasma Deposition And Titanium Dioxide Epitaxy

The present study suggest there is a possibility of plasma depositing single crystal thin films of titanium dioxide at lower temperatures than is required for CVD. Further work in this area is needed and should include additional studies of the effect of rf power, used during the deposition and the descum cycle, on the film structure.

Table 8. Prospective Reactants For Anion Incorporation Into Titanium Oxides By Plasma Enhanced Deposition

Anion	Reactants			Desired Product
Nitrogen	$\text{TiCl}_4 + \text{O}_2 + \text{NH}_3$			TiO_xN_y
Sulfur	"	"	SO_2	TiO_xS_y
"	"	"	H_2S	"
Phosphorous	"	"	PH_3	TiO_xP_y
Selenium	"	"	SeF_6	TiO_xSe_y
Tellurium	"	"	TeF_6	TiO_xTe_y

APPENDIX

Rotameter calibration

Lamp spectrum

X-ray diffraction data for anatase

X-ray diffraction data for rutile

Electron diffraction calculations

Experimental conditions used in series for
increasing anatase grain size

Computer program for parameter estimation

Computer calculations using data from Fig. 55

Computer calculations using data from Fig. 56

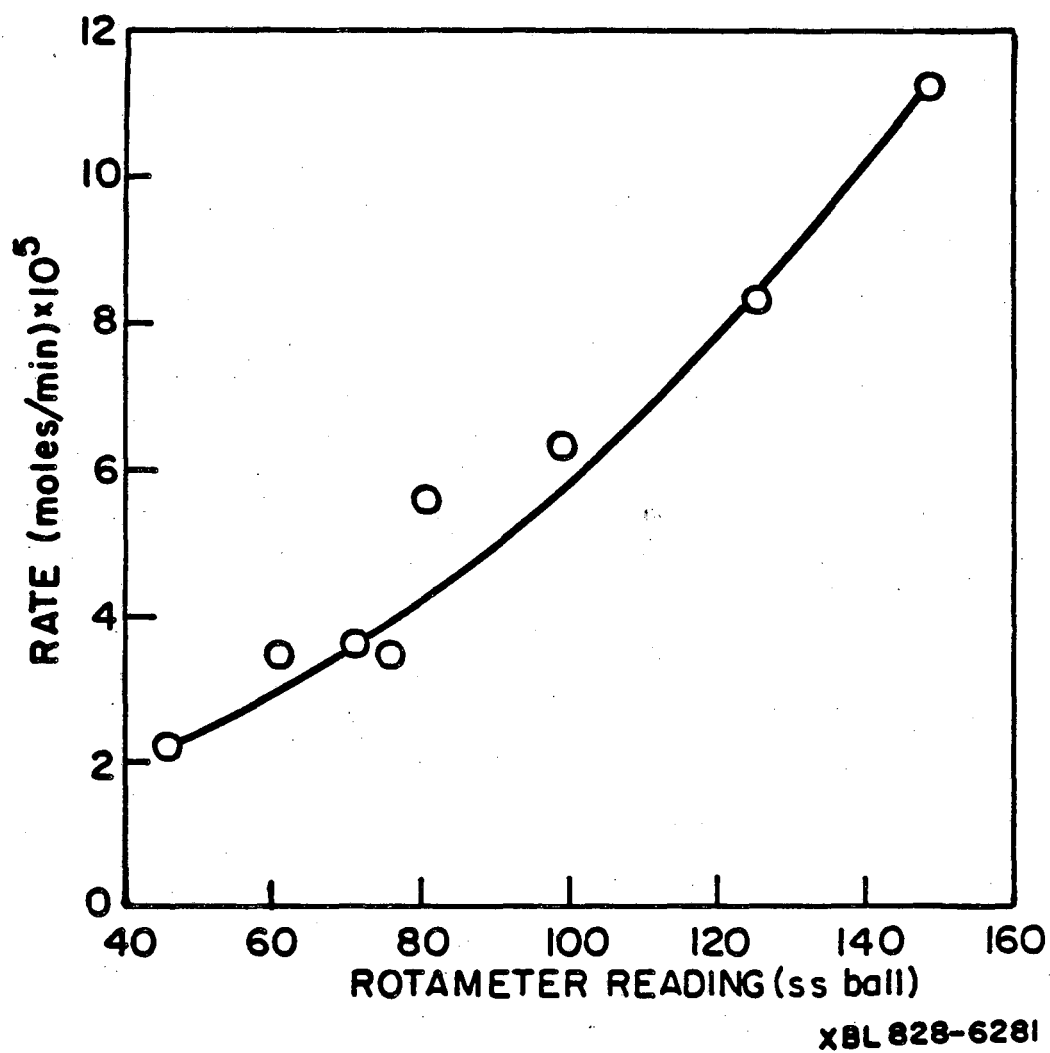


Fig. 62. Titanium tetrachloride rotameter calibration.

Table 9. Lamp Spectrum

Wavelength (nm)	Photon Flux (microamps/sq cm)
408	20.00
385	2.45
363	28.50
340	2.26
333	10.37
311	15.82
303	10.83
296	7.15
288	2.53
248	2.38

Table 10. X-Ray Diffraction Data For Anatase (132)

Bragg Angle 2 theta (deg)		d (A)	Relative Intensity	hkl
Cu k alpha	Fe k alpha			
25.3	31.9	3.52	100	101
37.0	47.0	2.431	10	103
37.8	48.1	2.378	20	004
38.6	49.1	2.332	10	112
48.1	61.6	1.892	35	200
53.9	69.4	1.700	20	105
55.1	71.0	1.667	20	211
62.1	80.9	1.493	4	213
62.7	81.7	1.481	14	204
68.8	90.5	1.364	6	116
70.4	92.7	1.338	6	220
74.1	98.3	1.280	2	107
75.1	99.9	1.265	10	215
76.1	101.5	1.251	4	301

Table 11. X-Ray Diffraction Data For Rutile (132)

Bragg Angle 2 theta (deg)		d (Å)	Relative Intensity	hkl
Cu k alpha	Fe k alpha			
27.4	34.7	3.25	100	110
36.1	45.8	2.487	50	101
39.2	49.9	2.297	8	200
41.2	52.5	2.188	25	111
44.1	56.3	2.054	10	210
54.3	70.0	1.688	60	211
56.6	73.2	1.624	20	220
62.8	81.8	1.480	10	002
64.0	83.6	1.453	10	310
65.5	85.7	1.424	2	221
69.0	90.8	1.360	20	301
69.8	92.0	1.346	12	112
72.4	95.9	1.304	2	311
76.5	102.2	1.244	4	202
79.8	107.5	1.201	2	212
82.3	111.7	1.170	6	321
84.2	115.0	1.148	4	400

Electron Diffraction Calculations

Methods for analyzing transmission electron diffraction patterns have been reported in the literature (86). The interplanar spacing can be obtained using the equation

$$Rd = \lambda L \quad (16.)$$

where R is the radius of the ring in the diffraction pattern, d is the interplanar spacing for that ring, λ is the wavelength of the electron beam, and L is the distance between the specimen and the photographic plate. The product of the wavelength and L is known as the camera constant. In the present study, the camera constant was determined using the diffraction pattern of an evaporated gold film and the reported d spacings (132). The camera constant was found to equal 1.707 angstrom - centimeters.

Table 12. Experimental Conditions Used In The Series For Increasing Anatase Grain Size

Deposition Temperature 400 C

No.	Descum Rf RF (watts)	Deposition RF (watts)	Titanium Tetrachloride (rotameter)	Oxygen (sccm)	He
1	10	10	77	8	no
2	10	10	77	1	no
3	100	10	77	8	no
4	100	10	77	1	no
5	10	10	60	1	no
6	10	10	95	1	no
7	5	5	77	1	no
8	0	10	77	1	no
9	5	5	77	8	no
10	5	5	65	1	no
11	100	5	65	1	no
12	5	5	80	1	yes
13	5	5	80	8	yes
14	5	5	52	1	yes
15	5	5	53	8	yes
16	5	5	82	1	yes
17	5	5	80	1	no
18	5	5	52	1	no

Computer Program For Parameter Estimation

```

100 REM *****
120 REM ***** SIMPLE SCHOTTKY MODEL *****
140 REM *****
160 REM *** NOTE LINES 100-120 GIVE SAMPLE DATA ***
220 PRINT "J"
240 PRINT "SIMPLE SCHOTTKY MODEL "
260 PRINT
280 PRINT "NUMBER OF KNOWN POINTS":
300 INPUT N
305 FOR I=1 TO N
306 READ PV(I):NEXT
309 DATA 0.0,0.1,0.2,0.3,0.4,0.5
312 FOR I=1 TO N
315 READ PI(I):NEXT
318 DATA .44,.46,.49,.51,.53,.55
320 REM ** INPUT "ARRAY NUMBER FOR FIRST POINT":FP
340 REM ** INPUT "ARRAY NUMBER FOR LAST POINT":LP
360 INPUT "PLATE AND ESTIMATE":FB
380 INPUT "PHOTON FLUX":PF
400 INPUT "WAVELENGTH":WL
420 INPUT "ABSORPTION COEFFICIENT":AC
440 INPUT "DIELECTRIC CONSTANT":DC
460 INPUT "NUMBER OF ITERATIONS":NI
480 J=0
500 K=0
520 L=0
540 M=0
560 R2=0
580 FOR C=1 TO N
600 CI(C)=PI(C)-DI(C)
620 CV(C)=PV(C)-FB
640 OE(C)=CI(C)/PF
660 YP(C)=LOG(1-OE(C))
680 XP(C)=CV(C)*10.5
700 X=XP(C)
720 Y=YP(C)
740 J=J+X
760 K=K+Y
780 L=L+X*Y
800 M=M+Y*Y
820 R2=R2+X*Y
840 NEXT C
860 B=(N*R2-K*J)/(N*L-J*Y)
880 A=(K-B*J)/N
900 NI=2*DC*8.854E-10*AC*Y/(1.602E-19*B*Y)
920 HL=(EXP(-A)-1)/AC
940 J=B*(R2-J*K/NI)
960 M=M-K*Y/NI
980 K=M-J
1000 PRINT
1020 R2=J/M
1040 IF NI=0 THEN 1260
1060 IF R2+.5<0.9800 THEN 1100
1080 GO TO 1260
1100 IF IN=NI THEN 1200
1120 PRINT "ITER NO. = ",IN,"CORR. =",SQ(R2)
1140 FB=FB+0.01
1160 IN=IN+1
1180 GO TO 480
1200 PRINT "*****"
1220 PRINT "***** DID NOT CONVERGE ***"
1240 PRINT "*****"

```



```

1260 PRINT PRINT "F(X) =" ; A ; " + (" ; B ; " * X)"
1280 PRINT "COEFFICIENT OF " ;
1300 PRINT "DETERMINATION"
1320 PRINT "(R^2) = " ; R2
1340 PRINT
1360 PRINT "COEFFICIENT OF " ;
1380 PRINT "CORRELATION = " ; SQR(R2)
1400 PRINT
1420 PRINT "STANDARD ERROR OF EST" ;
1440 PRINT "IMATE = " ; SQR(K / (N - 2))
1460 PRINT "CARRIER CONCENTRATION", ND, "PER CUBIC CENTIMETER" : PRINT
1480 PRINT "HOLE DIFFUSION LENGTH", HL, "CENTIMETERS" : PRINT
1500 PRINT "FLATBAND", FB, "VOLTS VS. SCE"
1520 PRINT : PRINT : PRINT
1540 INPUT "DO YOU WANT A HARD COPY? (0=NO, 1=YES)" : HC
1560 IF HC=0 THEN END
1580 PRINT : PRINT
1600 INPUT "TITLE FOR DATA ?" : T$
1620 OPEN 7, 4 : PRINT#7
1640 PRINT#7, T$ : PRINT#7 : PRINT#7 : PRINT#7, "SIMPLE SCHOTTKY MODEL"
1660 PRINT#7 : PRINT#7, "PHOTO FLUX", FF, "MICROAMPS PER SQ CM" : PRINT#7
1680 PRINT#7, "WAVELENGTH", WL, "NM" : PRINT#7
1685 PRINT#7, "ABSORPTION COEFFICIENT", AC, "PER CENTIMETER" : PRINT#7
1688 PRINT#7, "DIELECTRIC CONSTANT", DC : PRINT#7
1700 PRINT#7, "FLATBAND = " ; FB ; "VOLTS VS. SCE" : PRINT#7
1720 PRINT#7, "CARRIER CONCENTRATION", ND, "PER CUBIC CENTIMETER" : PRINT#7
1740 PRINT#7, "HOLE DIFFUSION LENGTH", HL, "CENTIMETERS" : PRINT#7
1760 PRINT#7, "Y = " ; B ; " * X + " ; A : PRINT#7
1780 PRINT#7, "COEFFICIENT OF " ;
1800 PRINT#7, "CORRELATION = " ; SQR(R2)
1820 PRINT#7
1840 PRINT#7, "STANDARD ERROR OF EST" ;
1860 PRINT#7, "IMATE = " ; SQR(K / (N - 2))
1880 PRINT#7, "COEFFICIENT OF " ;
1900 PRINT#7, "DETERMINATION"
1920 PRINT#7, "(R^2) = " ; R2
1940 PRINT#7 : PRINT#7 : PRINT#7, "DATA TABLE" : PRINT#7
1960 PRINT#7, "NUMBER", "POTENTIAL", "CURRENT", "FHI", "QE"
1980 PRINT#7
2000 FOR C=1 TO N
2020 PRINT#7, C, PV(C), CI(C), XP(C), QE(C)
2040 NEXT C
2060 CLOSE 7
2080 OPEN 7, 4 : CMD7 : LIST
READY.

```

Computer Calculations Using Data From Figure 55

SIMPLE SCHOTTKY MODEL

PHOTO FLUX 1 MICROAMPS PER SQ CM
 WAVELENGTH 333 NM
 ABSORPTION COEFFICIENT 170000 PER CENTIMETER
 DIELECTRIC CONSTANT 160
 FLATBAND = -.8 VOLTS VS. SCE
 CARRIER CONCENTRATION 1.30167614E+23 PER CUBIC CENTIMETER
 HOLE DIFFUSION LENGTH 3.67509964E-06 CENTIMETERS
 Y = -.626629652 * X + -.485364383
 COEFFICIENT OF CORRELATION= .998331881
 STANDARD ERROR OF ESTIMATE= 3.72268965E-03
 COEFFICIENT OF DETERMINATION
 (R12)= .996666543

DATA TABLE

NUMBER	POTENTIAL	CURRENT	PHI	QE
1	0	.65	.834427191	.65
2	.1	.66	.948683298	.66
3	.2	.67	1	.67
4	.3	.68	1.04680885	.68
5	.4	.69	1.09544512	.69
6	.5	.7	1.14017543	.7

Computer Calculations Using Data From Figure 56

DEP 146P

SIMPLE SCHOTTKY MODEL

PHOTO FLUX 1 MICROAMPS PER SQ CM
 WAVELENGTH 333 NM
 ABSORPTION COEFFICIENT 170000 PER CENTIMETER
 DIELECTRIC CONSTANT 160
 FLATBAND = -.82 VOLTS VS. SCE
 CARRIER CONCENTRATION 1.08914232E+24 PER CUBIC CENTIMETER
 HOLE DIFFUSION LENGTH 3.25487625E-06 CENTIMETERS
 Y = -.216830747 * X + -.440400345

COEFFICIENT OF CORRELATION= .967660357

STANDARD ERROR OF ESTIMATE= 5.74526103E-03

COEFFICIENT OF DETERMINATION

(R²)= .936366567

DATA TABLE

NUMBER	POTENTIAL	CURRENT	PHI	QE
1	0	.47	.905538514	.47
2	.1	.48	.959166305	.48
3	.2	.48	1.00995049	.48
4	.3	.49	1.05830053	.49
5	.4	.49	1.1045361	.49
6	.5	.5	1.14891253	.5

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