Lawrence Berkeley National Laboratory

Recent Work

Title

Occupied Electronic States of CaSi2 and CaSi: Soft X-Ray Fluorescence Spectroscopy

Permalink

https://escholarship.org/uc/item/5sp3q3h4

Journal

Physical Review B, 52(7)

Authors

Jia, J.J.
Callcott, T.A.
Asfaw, A.
et al.

Publication Date

1995-03-03

Lawrence Berkeley Laboratory
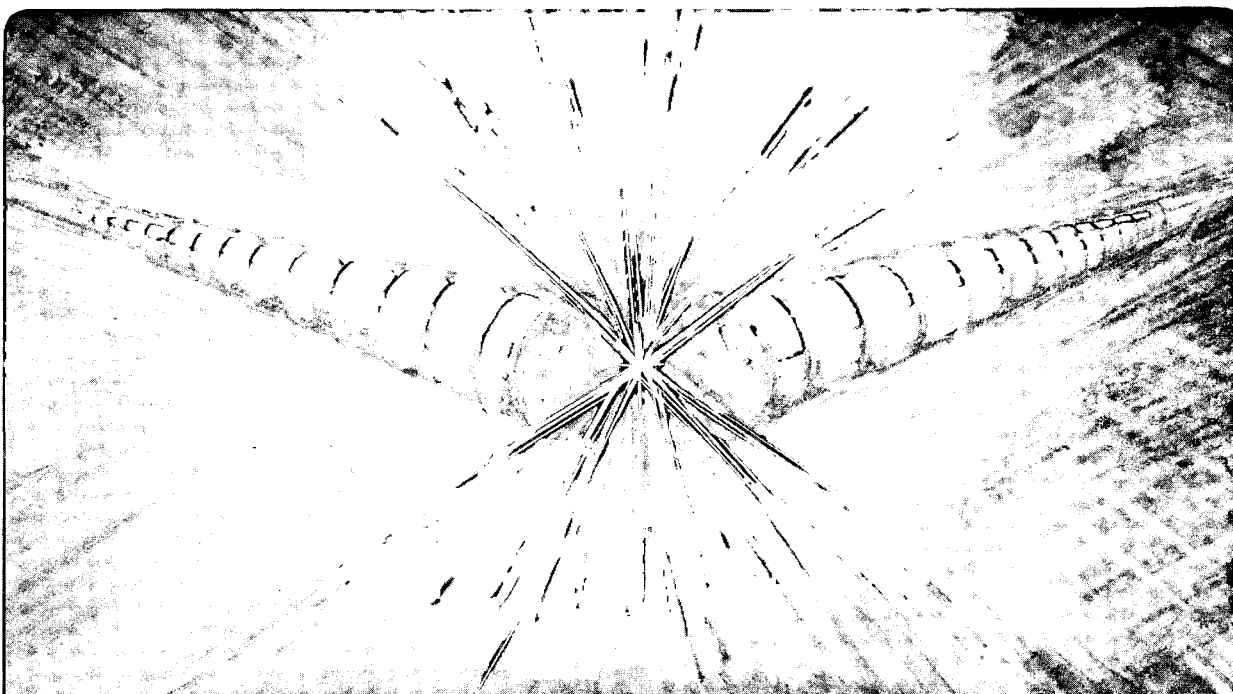
UNIVERSITY OF CALIFORNIA

Accelerator & Fusion Research Division

Occupied Electronic States of CaSi$_2$ and CaSi: Soft X-Ray Fluorescence Spectroscopy

J.J. Jia, T.A. Callcott, A. Asfaw, J.A. Carlisle, L.J. Terminello, D.L. Ederer, and R.C.C. Perera

March 1995

DISCLAIMER

OCCUPIED ELECTRONIC STATES OF CASI₂ AND CASI: SOFT X-RAY FLUORESCENCE SPECTROSCOPY*

J.J. Jia, T.A. Callcott
University of Tennessee
Knoxville, Tennessee 37996

A. Asfaw, J.A. Carlisle, L.J. Terminello
Lawrence Livermore National Laboratory
Livermore, CA 94551

D.L. Ederer
Tulane University
New Orleans, LA 70118

R.C.C. Perera
Advanced Light Source
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

March 3, 1995

Occupied electronic states of CaSi$_2$ and CaSi: soft X-ray fluorescence spectroscopy

J.J. Jia, T.A. Callcott
University of Tennessee, Knoxville, TN 37996

A. Asfaw, J.A. Carlisle, L.J. Terminello
Lawrence Livermore National Laboratory, Livermore, CA 94551

D.L. Ederer
Tulane University, New Orleans, LA 70118

R.C.C. Perera
Lawrence Berkeley Laboratory, Berkeley, CA 94720

Abstract

The Ca $L_{2,3}$ and Si $L_{2,3}$ fluorescence spectra for CaSi$_2$ and CaSi are studied. These spectra provide s and d partial density of states (PDOS) information for the Ca and Si atoms. The measured PDOSs are in good agreement with available calculations. Using monochromatized X-rays to excite core electrons to localized Ca d states near threshold produces resonant recombination fluorescence peaks for the L_3 and L_2 edges of Ca in both compounds. In CaSi, with resonant excitation, inelastic Raman peaks are also observed. The energy position of the inelastic peaks indicates that the creation of the core hole shifts the Ca d-states by several eV. The intensity of the resonance peaks indicates the degree of localization of the Ca d states, which is reduced by their participation in the bonding of the silicides. The empty Ca d states are found to be quite localized in CaSi, and less so in CaSi$_2$.

PACS numbers: 71.20.-b, 78.70. En

I. Introduction

CaSi$_2$ has been widely studied[1-5] because it is one of the few metalizing layers that can be epitaxially grown on the silicon surface. The studies of the electronic states of such materials can be beneficial, both for fundamental physics research and for improving technological applications. Bonding in transition metal silicides has generally been described in the framework of the hybridization between metal d and silicon p states,[6] though some theoretical[7,8] and experimental studies[9,10] have demonstrated that a full understanding requires consideration of s-p and s-d bonding as well. Calcium is an interesting case because it immediately precedes the transition metals in the periodic table so that the atomic d states are empty, but provide the lowest unfilled states in the atom. Thus understanding of the electronic structure of calcium silicides may be helpful to understanding other silicides in which the metals have partially filled d states.

Available experimental information on the occupied electronic states of these compounds has been obtained mainly from photoemission and Auger spectroscopy.[1-5] These methods have provided a large body of experimental information on the electronic density of states (DOS) of bulk silicides and Si-silicide interfaces. But they have certain disadvantages. For example, photoemission gives only a total density of states, and cannot usually resolve information either as to chemical element or angular momentum state. Auger spectra represent a complex convolution of the electronic density of states which can be difficult to interpret. Also, in Auger spectra, which have two holes in the final state, correlation effects have to be considered, which further complicates interpretation of the Auger spectral lineshape. In addition, electron spectroscopies place a stringent requirement on the cleanness of the sample surface and are less effective as a bulk probe.

Soft X-ray fluorescence (SXF) spectroscopy has proved to be a useful tool in providing electronic density of states information for crystalline materials.[9,10] The SXF spectra are capable of yielding site (Local) and angular momentum-specific (Partial) density of states (LPDOS) information for solid systems. It is a true bulk probe and less sensitive to surface contamination. It is not affected by sample charging, since photons rather than electrons are detected. The disadvantage of SXF spectroscopy is the typically low fluorescence yields for many core levels. Also many core levels have large lifetime and phonon broadening which limits the resolution of the spectra.

In this paper we present and discuss the Ca L$_{2,3}$ fluorescence spectra for both CaSi and CaSi$_2$, excited with monochromatic X-rays with energies just above the Ca L$_{2,3}$ absorption edge. We will show that the Ca d-states remain somewhat localized in silicides, more so in the CaSi than the CaSi$_2$. The large degree of localization inferred for CaSi indicates that the Ca d-states do not participate significantly in the bonding of this compound. In CaSi$_2$, the extra silicon atom increases the interaction between Ca and Si atoms, resulting in less localized Ca d states. The bonding must be described as a general hybridization between Si s-p states and the Ca s-p-d states for this silicide. We also will show the Si L$_{2,3}$ emission spectra of both silicides. The high energy shoulders of these Si spectra provide some information about the participation of silicon states in the bonding.

For both compounds, an elastic scattering peak is observed for resonant excitation into the Ca d-states. In CaSi, this peak is very strong and is accompanied by a spectral

feature at an energy 12 eV below, which we interpret as due to a resonant Raman scattering effect.

II. Experimental

Commercially available CaSi and $CaSi_2$ samples with 99.5% purity were used in the experiment. The SXF spectra were excited by photons from undulator beamline 8.0 at the Advanced Light Source (ALS) in Lawrence Berkeley Laboratory. Emitted photons were detected with a high efficiency fluorescence endstation recently constructed by the University of Tennessee, Knoxville.[11]

The SXF endstation consists of an ultrahigh vacuum sample chamber and a Rowland circle grating spectrometer. The emission spectrometer has a fixed entrance slit, four spherical diffraction gratings and a position sensitive area detector. The gratings are interchangeable from outside the vacuum. The detector is a true photon counting device utilizing microchannel plates and a resistive readout anode. Emission spectra are measured by positioning the detector along the Rowland circle to intercept the spectrum of interest, and utilizing the area detector to record the entire spectrum simultaneously. Scanning is accomplished by a precision X-Y-θ table on which the detector chamber is mounted. Both scanning and data acquisition are automated through an IEEE-488 bus interfaced to a personal computer.

All measurements reported here were made with an 100 μm entrance slit. The Ca $L_{2,3}$ spectra were obtained with a 1000 lines/mm, 10 meter radius grating. At the Ca L edge, the resolution is approximately 1.0 eV. The Si $L_{2,3}$ spectra were obtained with a 600 lines/mm, 5 meter radius grating. The resolution is estimated to be better than 0.3 eV.

Self-absorption can affect the emission spectra when absorption and emission spectra overlap. Corrections to emission spectra can be made with the knowledge of absorption information. However, self absorption is not believed to affect the spectral lineshape in our studies, though there are probably some effects on the magnitudes of the elastic resonance peaks. Our discussion of these peaks are qualitative in nature, thus no attempt was made to correct for self-absorption.

III. Results and discussion

a. Resonant elastic and inelastic scattering from Ca d states

The Ca $L_{2,3}$ spectra of CaSi and $CaSi_2$ are plotted in Figures 1 and 2. Several physical processes contribute to the spectral features displayed. Each spectrum is labeled with the photon energy used for its excitation. The "normal" fluorescence spectra, generated by the radiative recombination of Ca valence band states with the core hole, produce the spectral features that are centered near 343 eV and observed with "off resonance" excitation. These spectra will be discussed in the following section. Here we concentrate our attention on the resonant elastic and inelastic peaks that are excited near threshold.

Strong resonant elastic scattering peaks are observed in both compounds at excitation energies of about 348 eV and 351 eV. These peaks are produced when electrons are excited from the Ca $2p_{1/2}$ and $2p_{3/2}$ core levels to localized empty Ca d-states, and then radiatively recombine with the core states. This kind of resonance has also been

observed in many other systems where empty localized states exist in or just below the conduction band.[12-14] The localized states are also observed in absorption spectra, where they were attributed to Ca 2p-3d transitions.[15] Compared with the normal fluorescence peak at 343 eV (excited above the resonance at 358 eV), the resonance peak is almost 20 times stronger for CaSi and is only 7 times stronger for CaSi$_2$. Several factors account for the strength of this resonance. The p to d transitions are allowed by the dipole transition rule and consequently produce strong absorption. Also the d states, especially in the presence of the core hole, substantially retain their localized nature, despite their overlap with conduction band states. In fact, the coupling to delocalized states in the conduction band provides an alternative channel for the electrons, so that the stronger the coupling, the weaker the resonance peak will be. Hence a decreased magnitude of the resonance can be taken as a measure of increased inter-atomic bonding for the d-states. Clearly, the reduced intensity of the resonance in the di-silicide indicates stronger Ca-d interactions with the Si s and p states.

The "normal" fluorescence, visible between 339 and 345 eV is produced by transitions from valence states of s and d symmetry to the 2p core holes of Ca. In CaSi (Fig. 1), for on-resonance excitation at 348 eV, the normal fluorescence is suppressed and a broad peak emerges at energies between 332 and 338 eV, about 7 eV lower in energy than the "normal" fluorescence feature, and about 12 eV below the elastic peak. A similar displaced peak is visible, centered near 340 eV, for excitation into the second resonance at 351 eV, though the interpretation of this spectrum is complicated by overlap with the normal fluorescence. We have observed very similar resonant inelastic processes in CaF$_2$ and CaO,[16] and have reported similar results for hexagonal BN, where the resonance states are excitonic states derived from sp^2 π orbitals.[14] These displaced resonant peaks are attributed to the resonant inelastic scattering process in which the scattered photon loses part of its energy to a valence to conduction band type transition. This process may appropriately be described as an resonant Raman scattering process. This scattering process is resonant with a "spectator" fluorescence process, where the core hole is filled by a valence electron while the excited electron remains in a localized orbital as a spectator. The spectator electrons in the case of Ca silicides are the localized the 3d electrons. In both the inelastic scattering and spectator fluorescence processes, the final state is a valence hole and an excited electron. Making the reasonable assumption that the spectator electron remains in its d-orbital when the core hole is filled, the appearance of the inelastic resonance/spectator fluorescence peak about 7 eV below the normal fluorescence implies that the filling of the core hole results in a shift of the filled d-state by 7 eV. Shifts of similar magnitude are also observed in CaF$_2$ and CaO.[16] Though this shift is extraordinarily large, we have not been able to find any other explanation for the energy shift of the fluorescence spectra. We note that shifts between normal and spectator fluorescence spectra of 1.8 eV and 1.5 eV have previously been reported for resonant inelastic scattering in BN and B$_2$O$_3$.[13]

In Figure 2, we note that no prominent resonant inelastic peaks are resolved for CaSi$_2$, though a very weak displaced peak may be present centered at about 336 eV in the spectrum excited on the 348 eV resonance. The absence of the inelastic peak is consistent with both the reduced magnitude of the elastic resonance and the stronger Ca-d/Si-s and p bonding expected in the di-silicide.

4

b. The s+d density of states on Ca sites

We have noted above that the "normal" fluorescence spectrum provides a measure of the s+d local partial density of states (LPDOSs) on the Ca site. To discuss this density of states information, we choose the spectrum excited by 346.0 eV photons for CaSi (Fig.1) and the spectrum excited by 347.0 eV photons for $CaSi_2$ (Fig.2). These excitation energies are below the binding energies of the $2p_{1/2}$ core levels in either CaSi or $CaSi_2$, so they should give a clean L_3 spectrum which results from transitions from the valence states to the $2p_{3/2}$ core hole of Ca. However, in both of these spectra, there are still traces of the 3d - $2p_{3/2}$ elastic peak in the spectra. A Gaussian corresponding to the instrumental resolution was fitted to these spectra and the elastic peak was subtracted to give the pure L_3 spectra for both silicides, which are plotted in Fig.3. The Fermi energy is taken at 345.7 eV (ref. 15).

O. Bisi. et al. have calculated the electronic states of Ca silicides using the Andersen linear muffin-tin orbital method in the atomic-sphere approximation.[1] The calculation yields detailed information on the LPDOSs projected on both Ca and Si atoms. The Ca L_3 emission spectrum measures the (s+d) - LPDOS of the valence states on the Ca sites. Though the atomic d-states are empty, and most of the d-orbitals remain empty in the solid, the calculations indicate that states of d-symmetry make contributions to the valence band density of states comparable to that of the s-states. The principal qualitative difference between the two calculated LPDOSs is that the d-states peak at 1-2 eV below the Fermi level and the s-states peak at binding energies of about 4 eV. The oscillator strength of 3d - 2p transition is expected to be stronger than 4s - 2p transition since the 4s wave function is much more extended than that of the 3d wave function and does not overlap much with the 2p core hole. Thus we assume that the d type LPDOS makes the main contribution to the L_3 spectrum in our comparisons with theory, though there may in fact be some contributions from the s-states as well.

Comparison of our spectra with the projected Ca d-type density of states in the calculation yields good agreement in CaSi. The calculation gives the binding energy of the peak position of Ca d states just above -2 eV. The peak position in our spectrum is at -1.9 eV. The agreement in $CaSi_2$ is less satisfying. The calculation gives a peak position of around -2 eV while our spectrum puts it at close to -2.5 eV. The lineshape of the spectra seems to agree with the Ca d states in both silicides. The experimental spectra extend to binding energies of about -7 eV. The calculations show a total valence band width of about 12 eV, but the contributions to both d and s LPDOSs from Ca are very weak below about -5 eV, with most of the contributions at higher binding energies coming from the Si orbitals.

In Figs. 1. and 2, when the excitation energy exceeds 349 eV, there is additional emission intensity between 345 eV and 350 eV. This is the Ca L_2 emission. Particularly in $CaSi_2$, the L_2 emission peak is clear and strong for excitation energies between 349 eV and 353 eV, but is relatively weaker when the excitation energy is far above the L_2 threshold (Fig. 2). At 358 eV excitation, which is far above the Ca L edge, the L_2 emission is much weaker than the expected one half intensity of the L_3 emission. This indicates a Coster-Kronig type of non-radiative decay channel for the $2p_{1/2}$ core hole. The $2p_{1/2}$ hole quickly decays into a $2p_{2/3}$ core hole plus an ejected valence electron. An interesting observation is that L_2 emission seems to be enhanced near the L_2 resonance of the 2p - 3d excitation.

Such enhancement may have resulted from the suppression of Coster-Kronig process due to localized 3d spectator electron. Similar enhancements have been observed very near threshold in some other systems we have studied.

c. The s densities of states on Si sites

In Fig.4, the Si $L_{2,3}$ emission spectra of CaSi and CaSi$_2$ excited with 210 eV photons are shown. The Si L spectra provide a measure of the (s+d) LPDOS for Si atom in these silicides. The spectra can be divided into two regions for discussion. The region from 84 eV to about 94 eV lies well below the Fermi level and represents the non-bonding Si s electrons. The second region, from 94 eV to the Fermi level which is just below 100 eV in most silicides, gives information about the participation of s-electrons in the bonding of the silicides. The Si d states are well above s-p states and do not contribute significantly to the filled density of states. For complex structures like Ca silicides with very short inter-atomic distance, the Ca wavefunctions overlap onto the Si sites. If the combination of these atomic states have s or d type symmetry with respect to the Si atom with the excited core hole, then emission is possible as well. This is sometimes referred to as a crossover transition. The assignment of transition strengths to particular sites or orbitals is strongly dependent on the method of calculation and the basis functions assumed, so that the only unambiguous method of comparing experiment with theory is a full calculation that includes all symmetry effects in the computation of transition matrix elements. With this caution to the reader, we will compare our spectra to the calculations of Bisi et al.

These calculations indicate that the nonbonding Si s states of CaSi have an energy spread of about 5 eV. In CaSi$_2$, the Si atoms occupy two nonequivalent sites and the projected s-LPDOS are different for the two kinds of sites. The significant intensity distribution is from -12 eV to -5 eV for type I sites and is from -10 eV to -4 eV for type II sites (ref. 1). The emission spectra cannot distinguish the two different kinds of sites, and the observed emission spectrum sums contributions from type I and II sites. If we choose the crystalline Si $2p_{3/2}$ binding energy (99.8 eV) as the binding energy for these silicides, then the unbound part of Si s states seen in our spectra lies some 8 to 10 eV below the Fermi level for both silicides. The calculation yields a significant reduction for the width of unbound Si s electronic states going from CaSi$_2$ to CaSi. But in our spectra, only a slight decrease is observed. The spectral features representing nonbonding Si s states are split into peaks at 88 eV and 92 eV in both silicides, very reminiscent of the spectrum of crystalline Si. The splitting is generally derived from second nearest neighbor Si - Si interactions, and is absent in the spectrum of amorphous Si where only the local tetrahedral bonding (first nearest neighbor) is preserved.[10] The observation of this splitting of the main Si $L_{2,3}$ emission feature in these silicides proves that even though these Si s states are not much involved in the bonding of the silicides, the interaction from second nearest neighbor still exists.

The similarity of Si $L_{2,3}$ emission spectra of Ca silicides to the spectra of pure Si indicates that the covalent bonding in the elemental silicon is preserved in silicides. It is of importance to note that in both CaSi and CaSi$_2$, the nearest neighbors of a Si atom are not Ca but Si atoms (ref. 1). Covalent bonding is associated in the $L_{2,3}$ emission spectra of c:Si as a shoulder region above the unbound Si s states. We observe a similar shoulder in

6

the Ca silicides, extending from 94 eV up close to 100 eV. However the intensity of the shoulder region in CaSi and $CaSi_2$ is not as strong as in elemental Si. And it is less intense in CaSi than in $CaSi_2$, consistent with the fact that each Si atom has one less nearest neighbor Si atoms in CaSi than in $CaSi_2$.[17] Si L spectra retaining the characteristic features of tetrahedral covalent bonding have also been observed in the transition metal silicides of Fe, Co, and Ni.[9,10]

Close to the Fermi level, we observed a small peak at 97.9 eV for CaSi, and at 98.4 eV for $CaSi_2$. The projected partial density of states in Bisi's calculation show that the occupied Ca d states peak about 2 eV below the Fermi level. It is possible that these two small features arise as a result of the the overlapping of Ca d wavefunction onto the Si sites in these silicides, as similar peaks in the shoulder region have been observed in Si $L_{2,3}$ spectra of Ni and Co di-silicide.

References

1. O.Bisi, L. Braicovich, C. Carbone, I. Lindau, A. Iandelli, G. L. Olcese, and A. Palènzona, Phys. Rev. B **40**, 10194 (1989).
2. L. Calliari, F. Marchetti, M. Sancrotti, O. Bisi, A Iandelli, G. L. Olcese, and A. Palenzona, Phys. Rev. B **41**, 7569 (1990).
3. D. D. Sarma, W. Speier, L. Kumar, C. Carbone, A. Spinsanti, O. Bisi, A Iandelli, G. L. Olcese, and A. Palenzona, Z. Phys. B **71**, 69 (1988).
4. J. H. Weaver, A. Franciosi, and V. L. Moruzzi, Phys. Rev. B **29**, 3293 (1984).
5. C. Chemelli, M. Sancrotti, L. Braicovich, F. Ciccacci, O. Bisi, A Iandelli, G. L. Olcese, and A. Palenzona, Phys. Rev. B **40**, 10210 (1989).
6. C. Calandra, O. Bisi, and G. Ottaviani, Surf. Sci. Rep. **4**, 271 (1984).
7. D. Bylander, L. Kleinman, K. Mednick, and W. Grise, Phys. Rev. B **26**, 6479 (1982).
8. J. Tersoff, and D. Hamann, Phys. Rev. B **28**, 1168 (1982).
9. P. Weijs, G. Wiech, W. Zahorowski, W. Speier, J. Goedhoop, M. Czyzyk, J. van Acker, E. van Leuken, R. de Groot, G. van der Laan, D. Sarma, L. Kumar, K. Buschow, and J. Fuggle, Phys. Scr. **45**, 629 (1990).
10. J. J. Jia, T. A. Callcott, W. L. O'Brien, Q. Y. Dong, J.-E. Rubensson, D. R. Mueller, D. L. Ederer, and J. E. Rowe, Phys. Rev. B **43**, 4863 (1991).
11. J.J. Jia, T.A. Callcott, J. Yurkas, A.W. Ellis, F.J. Himpsel, M.G. Samant, J. Stohr, D.L. Ederer, J.A. Carlisle, E.A. Hudson, L.J. Terminello, D.K. Shuh, and R.C.C. Perera (to be published in Rev. Sci. Instrum.).
12. Y. Muramatsu, M. Oshima, and H. Kato, Phys. Rev. Lett. **71**, 448 (1993).
13. W. L. O'Brien, J. J. Jia, Q. Y. Dong, T. A. Callcott, K. E. Miyano, D. L.Ederer, D. R. Mueller, and C.-C. Kao, Phys. Rev. Lett. **70**, 238 (1993).
14. J.J. Jia, T.A. Callcott, J.A. Carlisle, L.J. Terminello, A. Asfaw, D.L. Ederer, F.J. Himpsel, and R.C.C. Perera (submitted to Phys. Rev. Lett.).
15. F.J. Himpsel, U.O. Karlsson, A.B. McLean, L.J. Terminello, F.M.F. de Groot, M. Abbate, J.C. Fuggle, J.A. Yarmoff, B.T. Thole, and G.A. Sawatzky, Phys. Rev. B **43**, 6899 (1991).
16. J. J. Jia et al. (unpublished).
17. W. B. Pearson, Handbook of Lattice Spacing and Structures of Metals and Alloys (Pergamon, New York, 1958)

Figure Captions

1. The Ca $L_{2,3}$ fluorescence spectra of CaSi excited by monochromatic photons of various energies near the Ca L edge. The numbers on top of each curve are the energies of the incident photons
2. The Ca $L_{2,3}$ fluorescence spectra of $CaSi_2$, with the exciation energies indicated.
3. The valence band emission spectra of CaSi and $CaSi_2$ stripped of elastic photon peak contribution. The Fermi energy is taken from ref. 9.
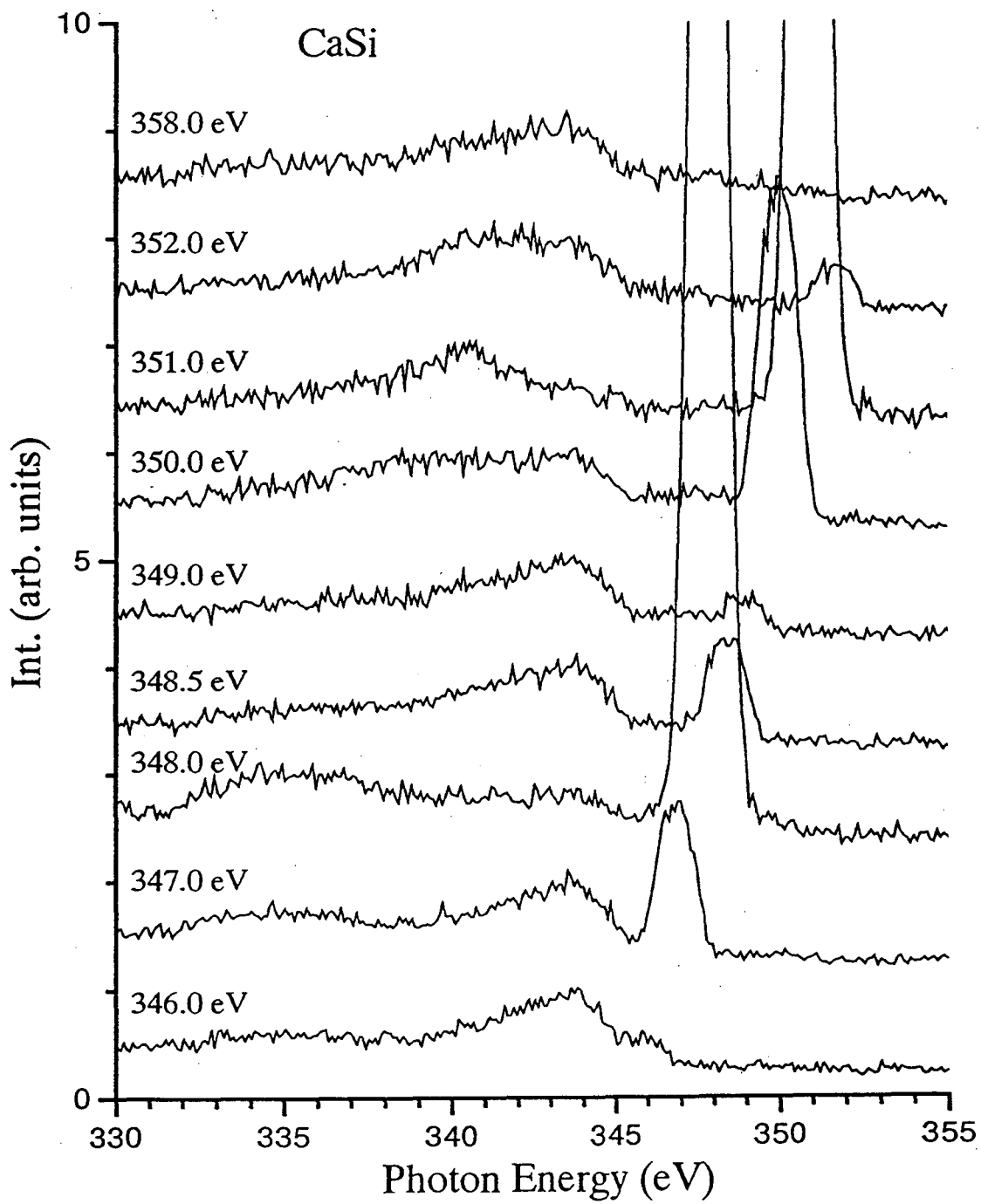4. The Si $L_{2,3}$ emission spectra of both CaSi and $CaSi_2$ excited by 210 eV monochromatic photons.
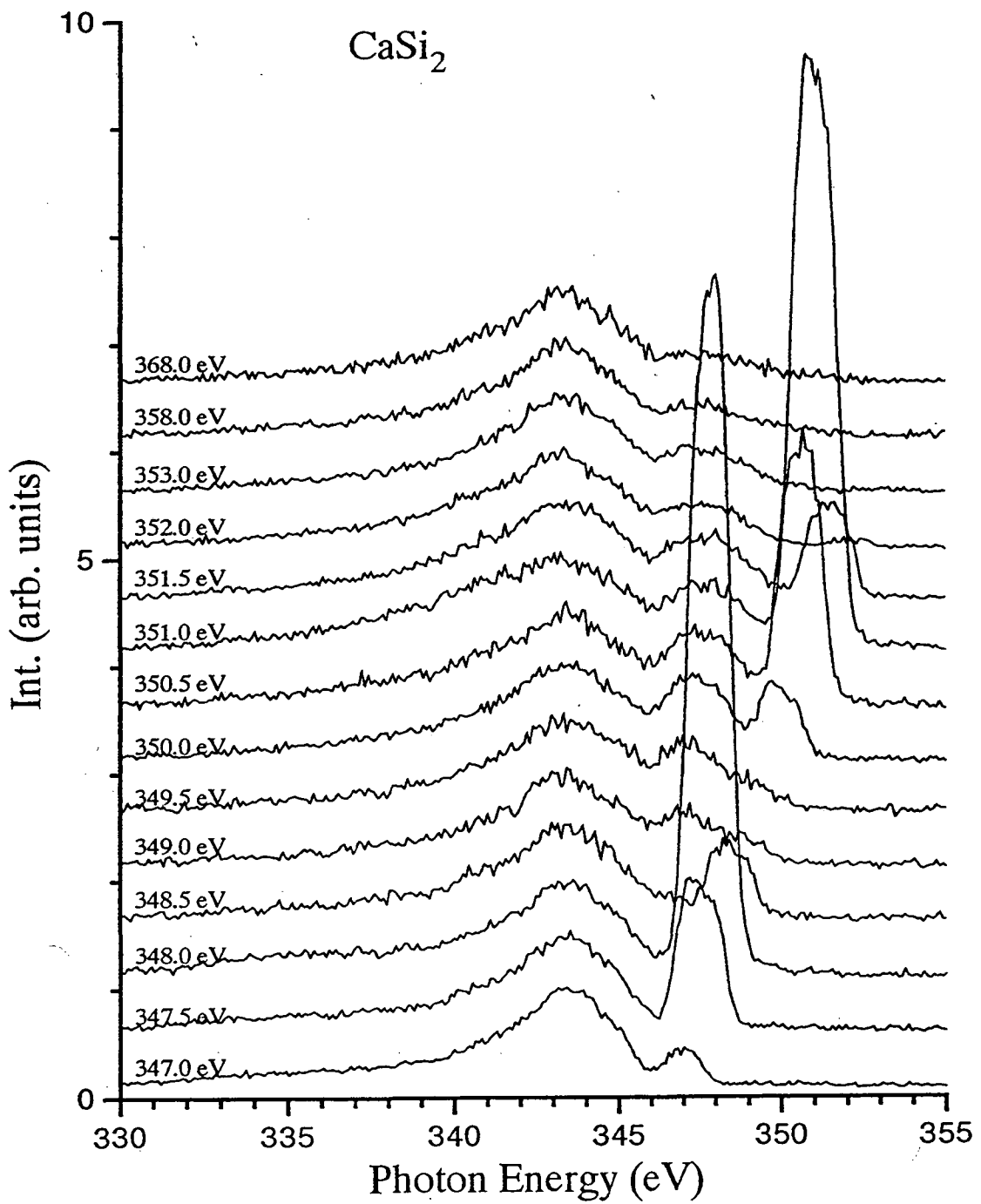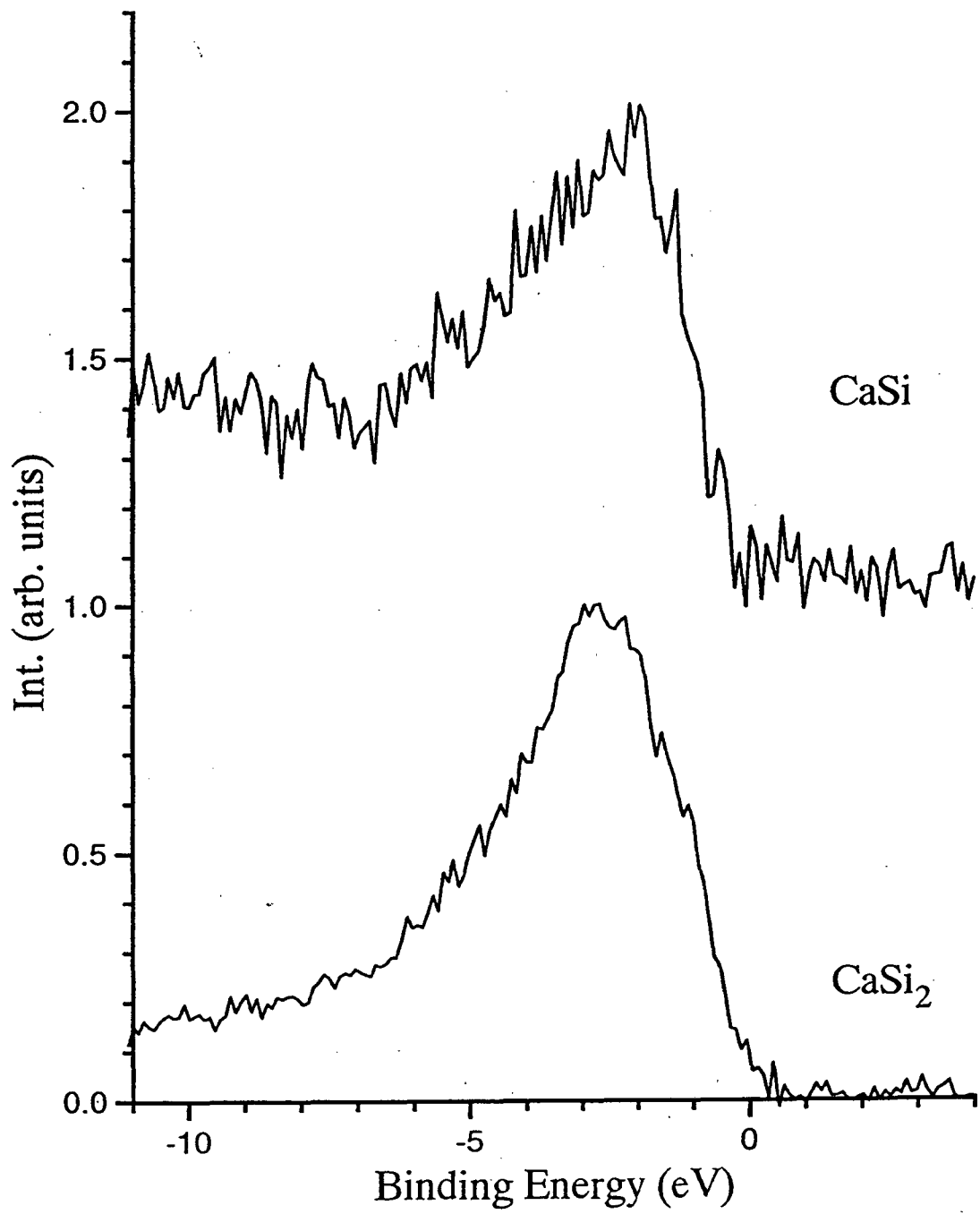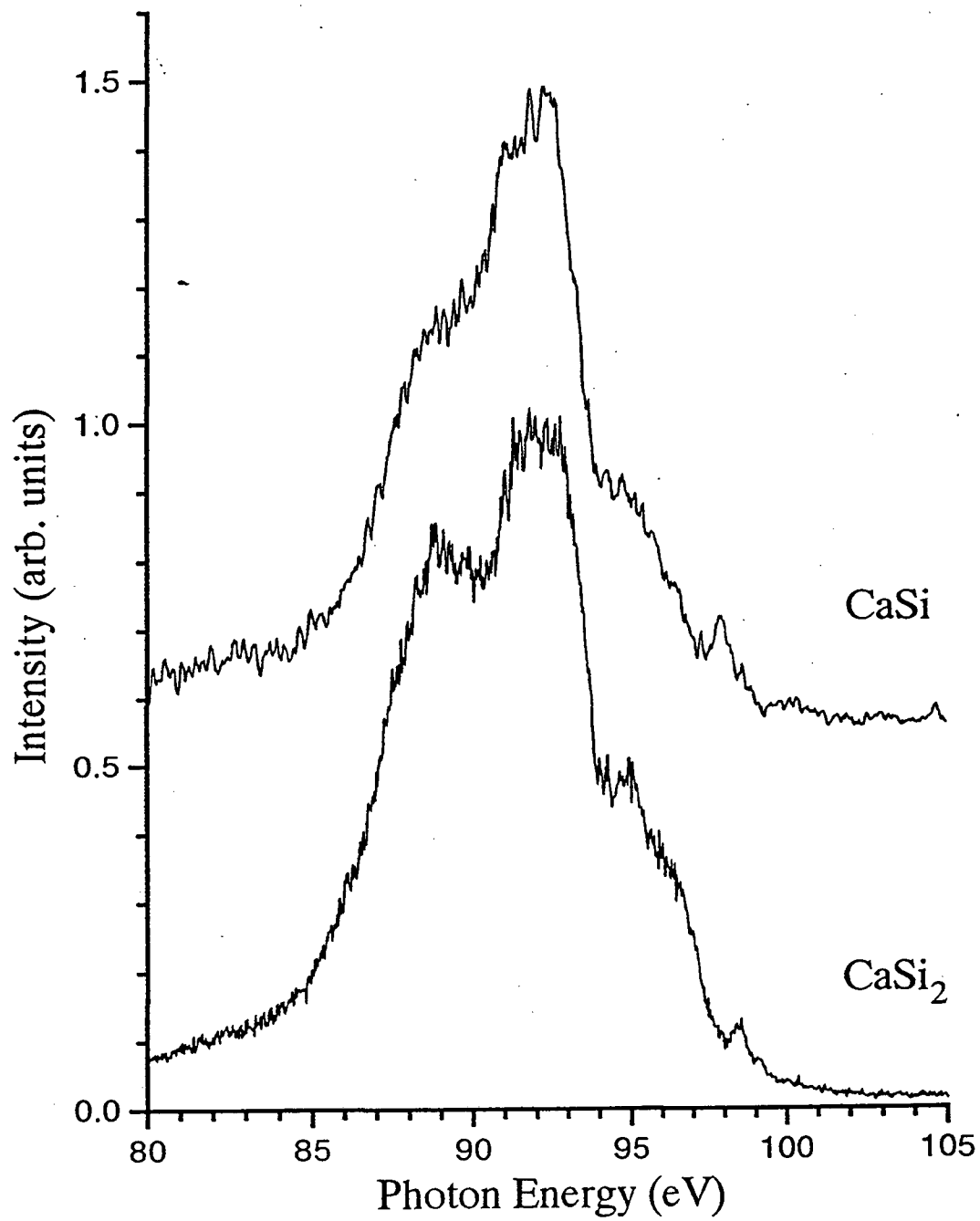
Fig. 1

Fig. 2

Fig. 3

Fig. 4

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL AND ELECTRONIC
  INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720