

## A PHOTOEMISSION STUDY OF Au, Ge, AND O<sub>2</sub> DEPOSITION ON NH<sub>4</sub>F ETCHED Si(111)

J. Terry, R. Cao, C. Wigren, and P. Pianetta  
Stanford Linear Accelerator Center

Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, CA 94309

### ABSTRACT

We have studied the interaction of a metal, Au, a semiconductor, Ge, and a non-metal, O<sub>2</sub>, with the NH<sub>4</sub>F etched Si(111) surface with photoemission spectroscopy. Two components were present in Si 2p core level spectra from the H-terminated surface. We observed the flat band condition from the as-etched, n-type, Si(111) surface. We performed stepwise depositions of Au and measured the band bending with photoemission spectroscopy. The Fermi level pinned near mid-gap as Au was deposited onto the as-etched surface. After the deposition of 1 ML of Au, a Au-silicide layer formed. This interfacial component indicated that the passivating H layer was compromised. As the Au coverage was increased, layers of pure Au formed between the bulk silicon and the Au-silicide layer. The observed behavior was nearly identical to that of Au deposition on the Si(111) 7x7 surface. Next, we tested the ability of the monohydride layer to sustain surfactant assisted growth of Ge. Ge islanding was observed at 400°C indicating that good surfactant growth was not obtained. This was consistent with the recent results of A. Sakai and T. Tatsumi, *Appl. Phys. Lett.* **61**, 52 (1994) who report that the surface roughness was nearly the same with or without H at this temperature. Although the monohydride layer was not a good surfactant for the Si(111) surface at this temperature, further study at different temperatures is needed to determine the ability of the ideal monohydride layer to act as a surfactant. Finally, we observed no oxidation of the as-etched surface at room temperature upon exposure to molecular oxygen.

### 1. INTRODUCTION

A standard method for preparing silicon surfaces has used HF etching to remove native oxide layers and to protect the surface from chemical attack. However, surfaces prepared in this manner are atomically rough. Due to the surface roughness, mono, di and trihydride species are present[1,2]. Recently, a method for preparing ideal H-terminated Si(111)

surfaces by chemically etching in aqueous NH<sub>4</sub>F solutions was developed[1, 2]. Infra-red spectroscopy has shown this surface to be terminated entirely by the monohydride and to be flat on an atomic scale[1, 2]. A high-resolution photoemission study of this surface showed that the Si 2p core level was very narrow, with a total linewidth of 0.160 eV, and that narrow features related to Si-H existed in the valence band[3]. These features

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in the core level and valence band spectra were much narrower than those previously reported for H-Si(111) prepared by H exposure in vacuum[4]. The discovery of this ideal H-terminated surface has opened up many possible avenues of study.

One area of study involves the interaction of metals with the passivated surface. Recent results of Hg deposition on this H-passivated surface have shown that the Hg/H-Si(111) interface behaves as an ideal Schottky diode[5,6]. The explanation offered for this behavior has the H termination layer remaining between the Hg and Si. In this position, H removes interface states responsible for the non-ideality of Schottky barrier heights. If Hg does not displace H, then it follows that H has the ability to prevent certain surface reactions. However, Wittmer and Freeouf[5,6] did not have a probe of surface reactions available to determine if a surface reaction occurred at the interface. They could only measure barrier height and so could not directly determine if Hg displaced H. Photoemission spectroscopy is an ideal probe of surface reactions and of the initial stage of Schottky barrier formation. We applied photoemission spectroscopy to investigate  $\text{NH}_4\text{F}$  etched surfaces that had been exposed to either a metal, Au, a semiconductor, Ge, or a nonmetal,  $\text{O}_2$ .

## 2. EXPERIMENTAL

The experiments were performed with the 6 m toroidal grating monochromator on Beam Line I-2 at the Stanford Synchrotron Radiation Laboratory. The experimental chamber was equipped with a VG ADES 400 angle resolved hemispherical analyzer with a combined resolution (analyzer and monochromator) of 0.37 eV at a photon energy of 130 eV. We used n-type, Si wafers that were cut in a (111) orientation with less than  $1^\circ$  miscut. These wafers were etched in a 40% solution of  $\text{NH}_4\text{F}$

by weight to produce the ideal H-terminated surface. After etching, the surface was rinsed for 10 seconds in deionized  $\text{H}_2\text{O}$  to remove residual compounds from the etching process. The samples were then introduced into the analysis chamber through our transfer system.

In this study, all depositions were performed at room temperature. Au and Ge were evaporated from tungsten filament evaporators. The depositions were monitored with a quartz crystal monitor that allowed us to determine coverages to an accuracy of 20%.  $\text{O}_2$  was introduced by backfilling the chamber to the designated pressure as measured with an ion gauge.  $\text{O}_2$  exposures were measured in Langmuirs. After  $\text{O}_2$  exposure the chamber was re-evacuated to the base pressure of  $1 \times 10^{-10}$  torr before any measurements were performed.

An electron beam heater was used to anneal the sample. The sample was slowly brought up to the desired temperature to minimize contamination from the sample holder which could not be outgassed prior to data collection. The pressure was held below  $5 \times 10^{-10}$  torr during all temperature ramping. The sample was held at the desired temperature for 10 minutes and then cooled to room temperature before any measurements were taken. The temperature was measured with a Chromel-Alumel thermocouple welded to the sample holder. The sample temperature had previously been calibrated to the thermocouple reading to within  $25^\circ\text{C}$  with an optical pyrometer.

The Si 2p core level spectra were decomposed according to a least squares fitting procedure that used doublets with a Voigt lineshape (Gaussian and Lorentzian). The least squares fit used a Lorentzian component of 0.07 eV, a branching ratio of 0.5, and a spin orbit splitting of 0.605 eV. These were the same parameters

used in Ref. 7. By varying the photon energy and in turn the kinetic energy of the photoelectrons we were able to change the surface sensitivity. In the case of silicon, the Si 2p core level spectra taken with photon energy of 130 eV are surface sensitive and those taken at 110 eV are bulk sensitive[4]. We then compared spectra taken with different surface sensitivity in order to determine the physical origin of the deconvolved components.

### 3. RESULTS and DISCUSSION

#### A. H-Si(111)

The lower spectrum in Figure 1A shows a surface sensitive,  $h\nu = 130$  eV, Si 2p core level spectrum from an  $\text{NH}_4\text{F}$  etched sample. The corresponding bulk sensitive spectra,  $h\nu = 110$  eV, is displayed in Figure 1B. The surface sensitive spectrum in Figure 1A was decomposed into two components according to the fitting procedure described above. The spectra from our etched samples were very similar to those previously reported by Karlsson, *et al.* [4] for H-Si(111). They attributed the first component to bulk silicon and the second, higher binding energy component to Si bonded to H[4]. Doubt was recently cast on this assignment by a high resolution study of  $\text{NH}_4\text{F}$  etched Si(111) by Hricovini, *et al* [3]. They observed three surface components, with very narrow Lorentzian linewidths (35 meV) in their Si 2p core level spectra, and assigned a peak shifted 0.14 eV to higher binding energy with respect to the bulk component to Si bonded to H. It appears that we did not have the resolution required to resolve the H-Si component from bulk silicon component. This suggests that the low binding energy component (29.8 eV Kinetic Energy) was a combination of the bulk Silicon component and the H-Si component and that the high binding energy component (29.5 eV Kinetic Energy), referred to as H1,

was a combination of the unassigned peaks of Hricovini, *et al* [3].

The component B of the Si 2p core level from H/Si(111) was shifted 0.50 eV to higher binding energy from the position of the bulk component of Si(111)7x7, not shown here. This corresponds to the Fermi level moving 0.50 eV toward the conduction band minimum from its pinned position on the Si(111)7x7 surface. Using the Fermi level position of the Si(111)7x7 surface, previously determined by Himpsel, *et al.*[10] to be  $E_F - E_V = 0.63$  eV, we determined that  $E_F - E_V = 1.13$  eV for the n-type,  $\text{NH}_4\text{F}$  etched Si(111) surface. As the Fermi level position was resonant with the conduction band minimum for silicon ( $E_C - E_V = 1.12$  eV), we concluded that the flat band condition was reached for  $\text{NH}_4\text{F}$  etched n-type Si. This is as we would expect if H quenches the surface states without adding any extrinsic states that could cause Fermi level pinning. So this behavior is consistent with the FTIR results[1,2] where H atoms were shown to quench the surface states of the Si(111)7x7 surface.

Figure 2 shows the valence band of  $\text{NH}_4\text{F}$  etched silicon taken with a photon energy of 27 eV. It was obvious that the  $\text{NH}_4\text{F}$  etching procedure saturated all dangling bonds at the surface due to the lack of photoemission intensity near the Fermi level. This was consistent with the previous FTIR and photoemission results from H-Si(111)[1-4]. By saturating the dangling bonds,  $\text{NH}_4\text{F}$  etching removed the most reactive sites and thus passivated the surface. We observed a peak at binding energy of 6.6 eV that was not found in spectra from clean silicon, therefore it must originate from a species formed during the etching process. Previous studies have observed features at 7 and 10 eV binding energies and assigned them to H-Si[11]. We followed this precedent and assigned the

observed feature at 6.6 eV to H-Si. This feature will be important in the following sections as it was used to determine the presence of hydrogen on the silicon surface. We could not positively identify a feature at 11 eV as due to H-Si, it is most like due to the overlap between a previously report H-Si peak[11] and a normal Si valence band feature.

## B. Au

We chose to study Au deposition on the  $\text{NH}_4\text{F}$  etched surface because the Au/Si(111) interface has been well characterized[8, 9]. These previous studies have shown that Au is very reactive towards silicon. With the initial Au deposition, a silicide layer formed. As the amount of Au deposited was increased, it diffused through the silicide layer and formed metallic Au layers between the silicide and the silicon substrate. The silicide was always observed to be at the vacuum interface. This well characterized system was invaluable for comparison purposes. Also, a previous study[13] had deposited Au on silicon surfaces previously exposed to atomic hydrogen. This study used electron energy loss spectroscopy (EELS) as a probe. EELS, unlike photoemission, is sensitive to hydrogen bonds. This study was also used for comparison purposes.

Figure 1 shows Si 2p core level spectra as a function of gold coverage. Here 1 ML ( $= 7.8 \times 10^{14}$  atoms/cm<sup>2</sup>) is defined as the number of surface Si atoms. Spectral decompositions are shown for the surface sensitive spectra (Figure 1A). We interpret the data by noting three different coverage regimes. For Au coverages  $\Theta < 0.7$  ML, only bulk sensitive Si 2p core level spectra and valence band spectra (Fig. 2) are shown. Throughout this coverage range, the deposition of Au caused the Si 2p linewidth to become slightly broader than that from H/Si(111). Because the Si 2p lineshape was only

slightly changed, it was likely that Si-H bonds were still present at low Au coverages. The intensity of the bulk component decreased exponentially as the Au was deposited. The exponential decrease of the Si 2p bulk component intensity can be explained using a simple two layer model where the intensity would be expected to decrease as  $\exp(-d/\lambda)$  where  $d$  is the distance from the surface and  $\lambda$  is the escape depth of the photoelectrons. The exponential attenuation of the core level strongly suggested that Au did not form clusters on the surface.

The valence band spectrum was unchanged throughout this coverage region. The Si-H peak at 6.6 eV still showed strong emission. Using this information and the core level data described above, it can be seen that at these low coverages of Au, Si-H bonds were present. The valence band spectra show no emission near the Fermi level so at low coverage we cannot detect any metallic clusters.

The bulk sensitive core level shifted to lower binding energy (higher kinetic energy) as Au was deposited. The energy position of the bulk component centroid has been marked to make this progression easier to follow. This motion of the core level was entirely due to band bending. After the deposition of 0.1 ML Au, the bulk component shifted 0.5 eV. As discussed above, this signifies that the Fermi level moved 0.5 eV toward mid-gap. One possible explanation for the Fermi level movement could be formation of interface states causing Fermi level pinning. A second explanation could have the H remaining between the Au and the Si surface, where it might prevent the formation of interface states. In this case, the Fermi level motion would be caused by the formation of an ideal Schottky barrier where the shift is caused by the work function of Au. Wittmer and Freeouf[5,6] may have observed a Schottky barrier of this type.

However, since we evaporate Au onto the surface, we must consider the effect of the heat of condensation on the passivation layer. This is an effect the Wittmer and Freeouf avoided by exposing their surface to liquid Hg. The energy imparted to the surface during condensation would be expected to destabilize the passivation layer. Also, the observed band bending was similar to that observed for low coverages of Au on the Si(111)7x7 surface[8] where interface states cause Fermi level motion. We believe that the passivation layer was compromised during Au deposition and that interface states formed which caused Fermi level pinning near mid-gap.

For Au coverages  $0.7 \text{ ML} \leq \Theta \leq 7 \text{ ML}$ , we began to observe a new component in the surface sensitive Si 2p spectra (Figure 1A). The two components in these spectra are labeled B and S. By comparing bulk and surface sensitive spectra, we determined component B to originate from photoemission from bulk silicon and component S from emission from silicon atoms that had reacted with Au to form a silicide. The composition of the Au silicide on the Si(111)7x7 surface has previously been determined to be  $\text{Au}_3\text{Si}$ [8,9]. The emission from the silicide layer was initially shifted 0.55 eV to higher binding energy relative to the bulk component. The shift to higher binding energy implies that charge was transferred from silicon to Au. However, the energy splitting between the silicide (S) and the bulk component (B) was not constant, it increased to a maximum observable splitting of 0.64 eV with increasing Au coverage. This indicated that the silicide composition was not uniform. The previously determined composition,  $\text{Au}_3\text{Si}$ , was a mean composition of the silicide layer.

The intensity of component (S) increased until the maximum intensity was reached after deposition of 7 ML Au. Intensity analysis

showed that the silicide contained between 1 and 2 ML of reacted silicon. These results were consistent with those from the deposition of Au on the Si(111)7x7 surface. There, the silicide was reported to stabilize after the deposition of 6 ML Au and to consist of 1 to 1.5 ML of reacted Si[8,9]. The bulk component intensity continued to decrease exponentially as was observed at low coverages, which clearly indicates that Au was uniformly deposited on the surface. The bulk component (B) shifted further to lower binding energy due to increasing band bending. The band bending continued to increase up to a Au coverage of 7 ML when the bulk signal was last observed (Fig. 1B). The data does show that the band bending was nearing saturation at this point. The fact that the band bending increased at high coverages is different from that of Au deposition on the Si(111)7x7 surface where the band bending stabilized at a Au coverage of 2 ML[8,9]. While the rate at which the band bending saturated was different, the final pinning positions were similar. We surmise that the mechanism of Schottky barrier formation was the same for both surfaces because the final pinning positions were similar.

Figure 2 shows the valence band taken with photon energy of 27 eV. We made two interesting observations here. First, photoemission intensity increased near the Fermi level which indicated the formation of metallic layers. Second, the spin-orbit splitting between the two peaks of the Au 5d doublet near 5 and 7 eV increased with the Au coverage. This progression has been marked in Figure 2. This splitting began with a value of 1.4 eV which is near the value (1.5 eV) observed from atomic Au[12]. The increase of the Au 5d spin orbit splitting reflects evolution from atomic Au to metallic Au as coverage was increased. The final feature to notice in the valence band is at 6.6 eV, the H-Si peak

described above. This feature overlapped with the Au 5d<sub>3/2</sub> component so it could not be used to determine the presence of Si-H bonds. Because of this and the fact that we could not resolve the Si-H shift in the Si 2p core level spectra, we rely on the results of an earlier study[13] that used EELS, which is sensitive to H, and Auger spectroscopy to investigate Au deposition on a Si(111) surface that had been exposed to atomic hydrogen. Iwami, *et al.* [13] found that Si-H bonds were present until 5 ML of Au had been deposited. It appeared that some Si-H bonds remained at the Au-Si substrate interface, although, because a silicide was formed it was extremely unlikely that the uniform passivation layer that we started with remained intact.

For Au coverages  $\Theta \geq 7$  ML, the bulk component was completely attenuated. A new component (S1) shifted 0.66 eV to higher binding energy relative to the silicide component (S) appeared in the surface sensitive spectra. This component was not observed for the Au/Si(111) system. As we discussed earlier, the chemical shift of the silicide peak was due to charge transfer from silicon to gold atoms. Chemical shifts depend upon the number of surrounding atoms. This implies that a new species with more Au surrounding the silicon atoms forms at high coverage. The silicide component (S) was attenuated as the S1 component increased. These findings strongly indicate that some Si atoms from the silicide dissolved in the Au layers. This is consistent with the higher binding energy of the S1 component.

Si 2p core level emission was observed after the deposition of 70 ML of Au, therefore the silicide layer did remain on the surface. The silicide which we previously determined to consist of approximately 1 ML of silicon could only consist of 2-3 ML of reacted Au with composition Au<sub>3</sub>Si. Therefore, the majority of

deposited Au must have existed in metallic layers underneath the silicide. This is consistent with results from Au deposition on Si(111)7x7. In the valence band spectra, strong emission near the Fermi level indicated the existence of metallic layers. The Au 5d spin-orbit splitting reached a maximum value of 2.4 eV. This value was identical to the splitting observed from metallic Au[12]. Using the spin-orbit splitting data and the data on the amount of silicide present, it was natural for us to conclude that the majority of Au was deposited in a metallic state.

For Au coverages  $\Theta < 0.7$  ML, we observed that a uniform layer of Au was formed on the surface. Silicon-hydrogen bonds were also detected. There was no evidence to suggest that a Au-Si reaction occurred at these low coverages. However, we observed significant band bending which was most likely the result of the formation of interface states causing the Fermi level to move toward mid-gap. In the coverage region,  $0.7 \text{ ML} \leq \Theta \leq 7 \text{ ML}$ , we observed the formation of a Au-silicide layer. The Au was originally deposited onto the Si surface in an atomic-like manner. As more Au was deposited, metallic layers of Au were formed. The layers of silicide and metallic Au attenuated the bulk signal exponentially. The composition of the silicide was not uniform because the energy splitting between the silicide component and the bulk component was not constant. These results are consistent with those previously observed for Au/Si(111)[8,9,13]. However, the band bending continued to increase throughout this coverage range. This is different from Au deposition on Si(111)7x7 where the band bending saturated at lower coverage. It was clear that the band bending was nearing saturation at  $\Theta = 7$  ML at a value similar to that of the Au/Si(111) system. This implied that the mechanism for Schottky barrier formation was similar whether or not H was present. An earlier

study[13] observed Si-H bonds to Au coverages of 5 ML and we find no evidence to dispute this result. In the coverage region,  $\Theta \geq 7$  ML, a thick metallic Au film formed. The silicide and metallic Au layers completely attenuated the bulk signal. However, Si 2p core level emission was still observed at high coverage. This emission must have originated from silicide atoms residing on top of the thick metallic Au film. Also, a Si 2p component never before observed was attributed to Si dissolved in the metallic Au. We determined that the dissolved silicon atoms came from the silicide layer due to attenuation of the silicide component. This system consisted of 2-3 ML layers of Au-silicide above a thick film of Au that sat on top of the bulk silicon. It is likely that some hydrogen was still present at the interface between the metallic Au and Si. The presence of the original monohydride layer did not appear to inhibit the interaction between Au and Si.

### C. Ge

Studies [16 and ref. therein] have shown that Sb and other species that saturate the dangling bonds on silicon surfaces act as surfactants. Surfactants minimize surface energy and provide a growth front for Ge on Si. The presence of a surfactant transforms the growth from Stranski-Krastanov mode, 1-2 layers followed by island growth, to layer by layer growth. Since the monohydride saturates dangling bonds on the silicon surface and provides a uniform starting surface, we were interested in determining if the monohydride layer would act as a surfactant on the Si(111) surface.

Figure 3 shows surface sensitive Si 2p core level spectra. These spectra were taken with various coverages of Ge and were normalized to maximum intensity. We observed no changes in Si 2p lineshape as Ge was deposited at room temperature. The observed peak to

valley ratio was constant within our experimental error. This was not surprising as no Ge-Si component has previously been observed in the Si 2p core level from Ge-Si interfaces formed under different conditions[7,15-17]. However, since the lineshape after deposition was identical to that from H-Si(111), it is likely that Si-H bonds still exist at the interface. As the sample was annealed to 400 °C, the Si 2p core level decreased in linewidth. Since we believe that the core level was a combination of Si-H and bulk Si, the decrease in linewidth implies that the Si-H bonds were destroyed. These bonds were destroyed well below the monohydride desorption temperature (530 °C) on the Si(111) surface[18]. The hydrogen would not be expected to remain on the Ge surface as the annealing temperature was above the monohydride desorption temperature (150 °C) on the Ge(111) surface[19].

Figure 4 shows the corresponding bulk sensitive Si 2p core level spectra. The Si 2p core level showed a large increase in intensity after annealing. The only possible explanations for this increase in core level intensity are Ge islanding, Ge desorption, or Ge dissolution. The Ge 3d core level, not shown here, was initially very broad. After annealing it had narrowed enough that the spin-orbit splitting was observed. This is indicative of ordering of the Ge layer. The Ge 3d peak did not show much change in intensity after annealing. Annealing at 400 °C does not cause significant Ge desorption, which leaves only islanding and dissolution as possible causes for the growth of the Si 2p intensity.

The bulk sensitive Si 2p spectra in Fig. 4 have had the bulk component aligned to compensate for band bending. Clearly seen in this figure was the fact that the Si 2p core level after annealing was much narrower than that from the H-terminated surface. Narrowing of the Si

2p core level has previously been determined to be caused by the formation of uniform Ge layers that force the Si atoms into a bulk-like environment[8,16,17]. We conclude that after annealing 1-2 uniform layers of Ge are formed on the surface with Ge islands above these uniform layers. These results are consistent with a recent high resolution transmission electron microscopy study of Ge growth on Si using atomic H as a surfactant[20].

#### D. O<sub>2</sub>

We exposed the sample to oxygen to determine how well the sample was passivated by the H-layer. The Si 2p core level spectra from samples exposed to oxygen are not shown here. No evidence of oxidation was evident up to O<sub>2</sub> exposures of 100,000 L. This was in contrast to the observed behavior as O<sub>2</sub> was exposed to the clean Si(111)7x7 surface. In these studies[14], exposure to as little as 0.1 L O<sub>2</sub> resulted in surface oxidation. As this study was performed with an ion gauge filament turned on, some atomic oxygen must have been formed. No evidence of oxidation was evident even with some exposure to atomic oxygen. We find that the as-etched surface has remarkable passivation ability against oxidation.

#### 4. CONCLUSION

In summary, we observed the flat band condition for NH<sub>4</sub>F etched n-type Si. As Au was first deposited a uniform layer of atomic-like Au formed on the surface. Silicon-hydrogen bonds were still present on the surface. The Fermi level pinned near mid-gap most likely as the result of the formation of interface states. At intermediate Au coverages, a Au-silicide layer approximately 2-3 ML thick formed. The composition of the silicide was not uniform. The remaining Au formed a metallic layer between the silicide and the silicon surface.

Previous results[13] suggested that silicon-hydride bonds could be found at the metallic Au -Si substrate interface. This interface then would be non-uniform. At high coverages, the silicide and metallic Au layers attenuated the bulk signal. The Si 2p core level emission still observed was predominately from the silicide layers which remained above the metallic Au film. The remaining Si 2p emission was attributed to Si atoms from the silicide that dissolved in the metallic Au. This system was observed to consist of 2-3 ML layers of Au-silicide above a thick film of Au that sat directly on top of the bulk silicon. As Ge was deposited uniform, amorphous layers formed on top of the H-Si(111) surface. The Si-H bonds were not significantly affected by Ge deposition. Moderate annealing led to the formation of ordered Ge islands on top of 1-2 uniform layers of Ge above the Si surface. This was not very different from direct deposition of Ge on a clean silicon surface. There was no evidence of Ge-H formation, this was not unexpected as the annealing temperature was above the monohydride desorption temperature from Ge(111). We concluded that a monohydride layer did not behave as a surfactant on the Si(111) surface at temperatures above 400°C which was consistent with the recent results of Sakai and Tatsumij[20]. Finally, no oxidation of the H-terminated surface was observed after exposures as high as 100,000 L O<sub>2</sub>.

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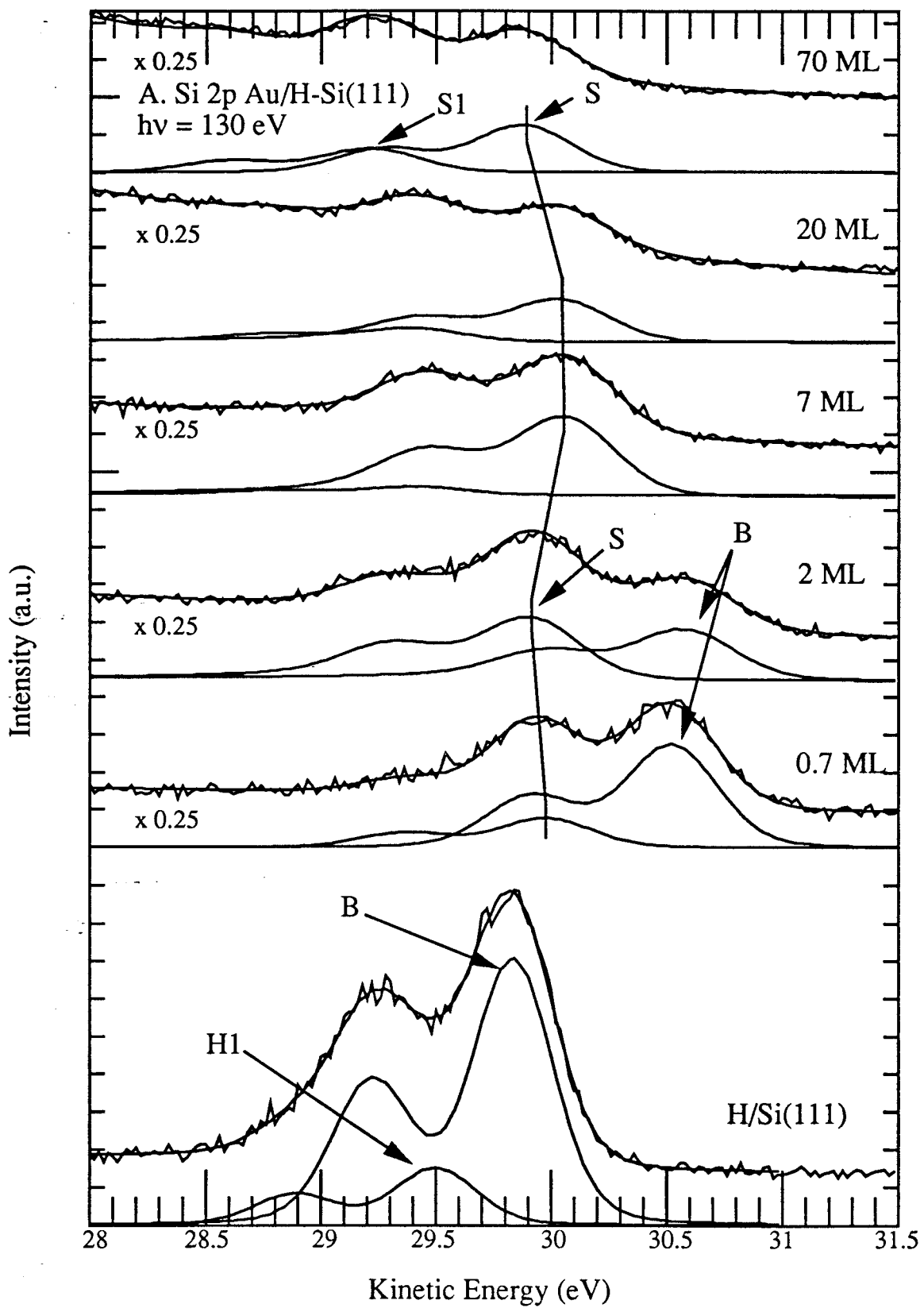


Figure 1: Si 2p core level spectra (1A:  $h\nu = 130$  eV, 1B:  $h\nu = 110$  eV) with difference Au coverages are shown. Some spectra have been taken at different pass energy and scaled to fit in the figure. The labeled features are discussed in the text.

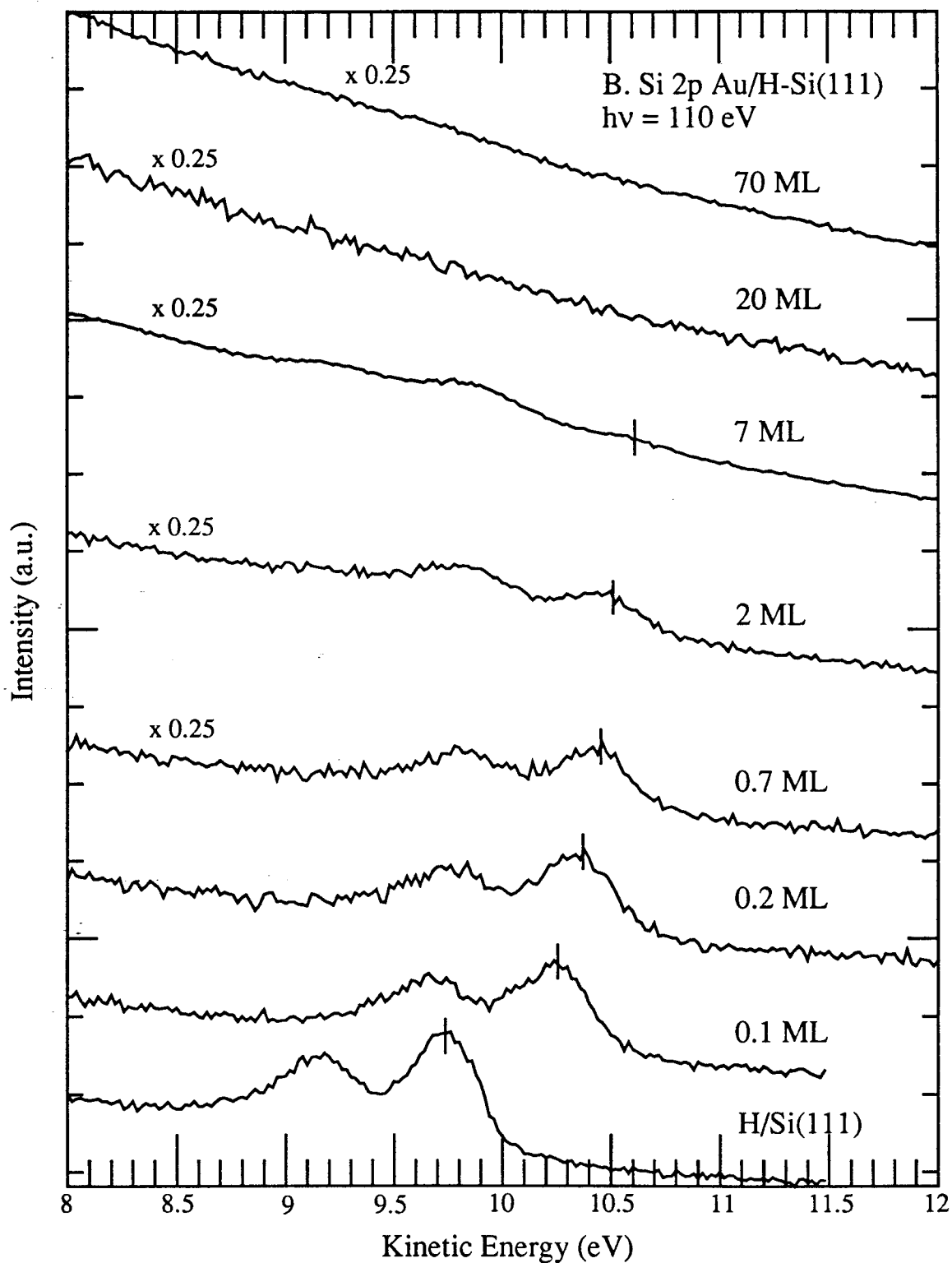


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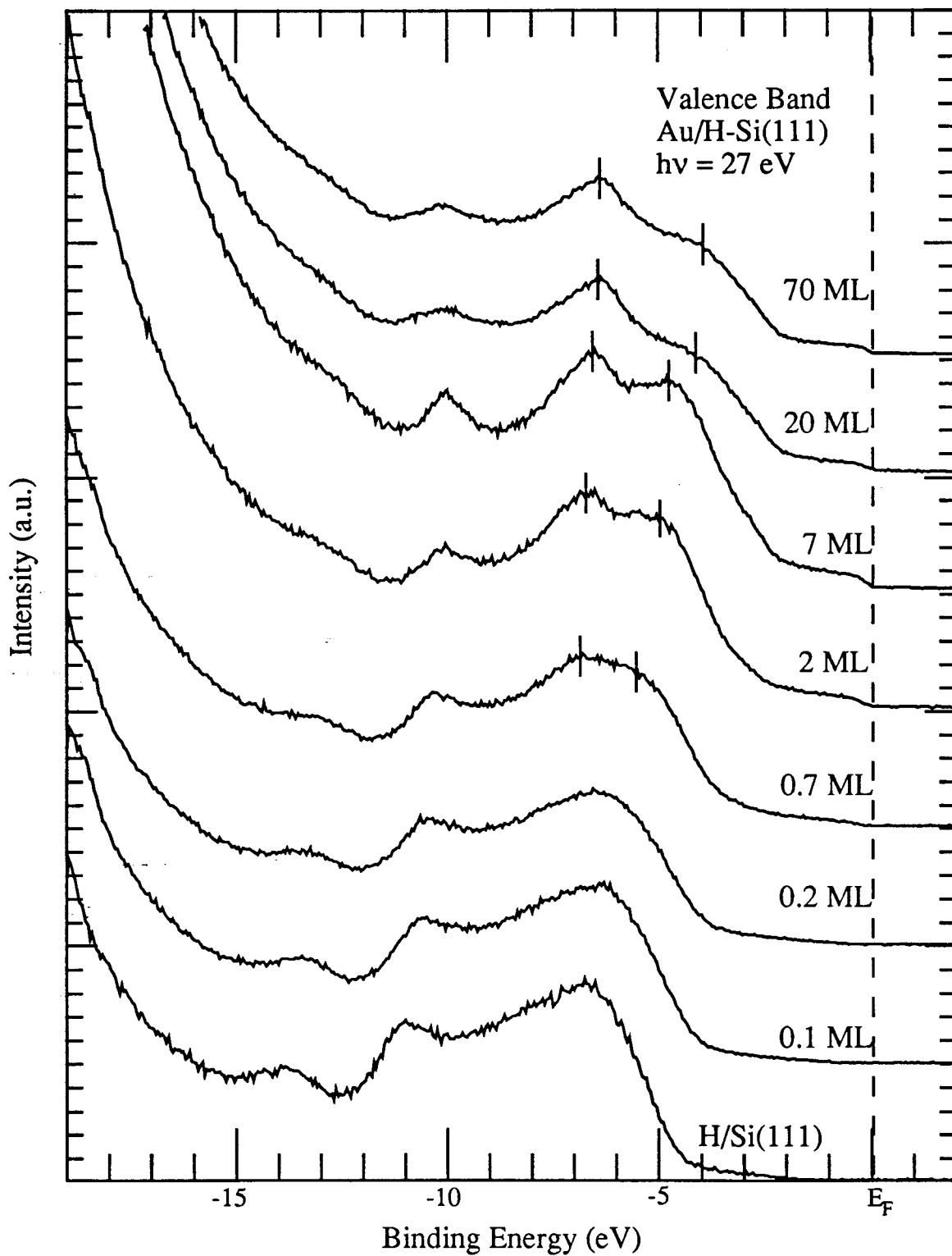


Figure 2: Valence band spectra ( $h\nu = 27$  eV,  $\Theta = 0$ ) with different Au coverages are shown.

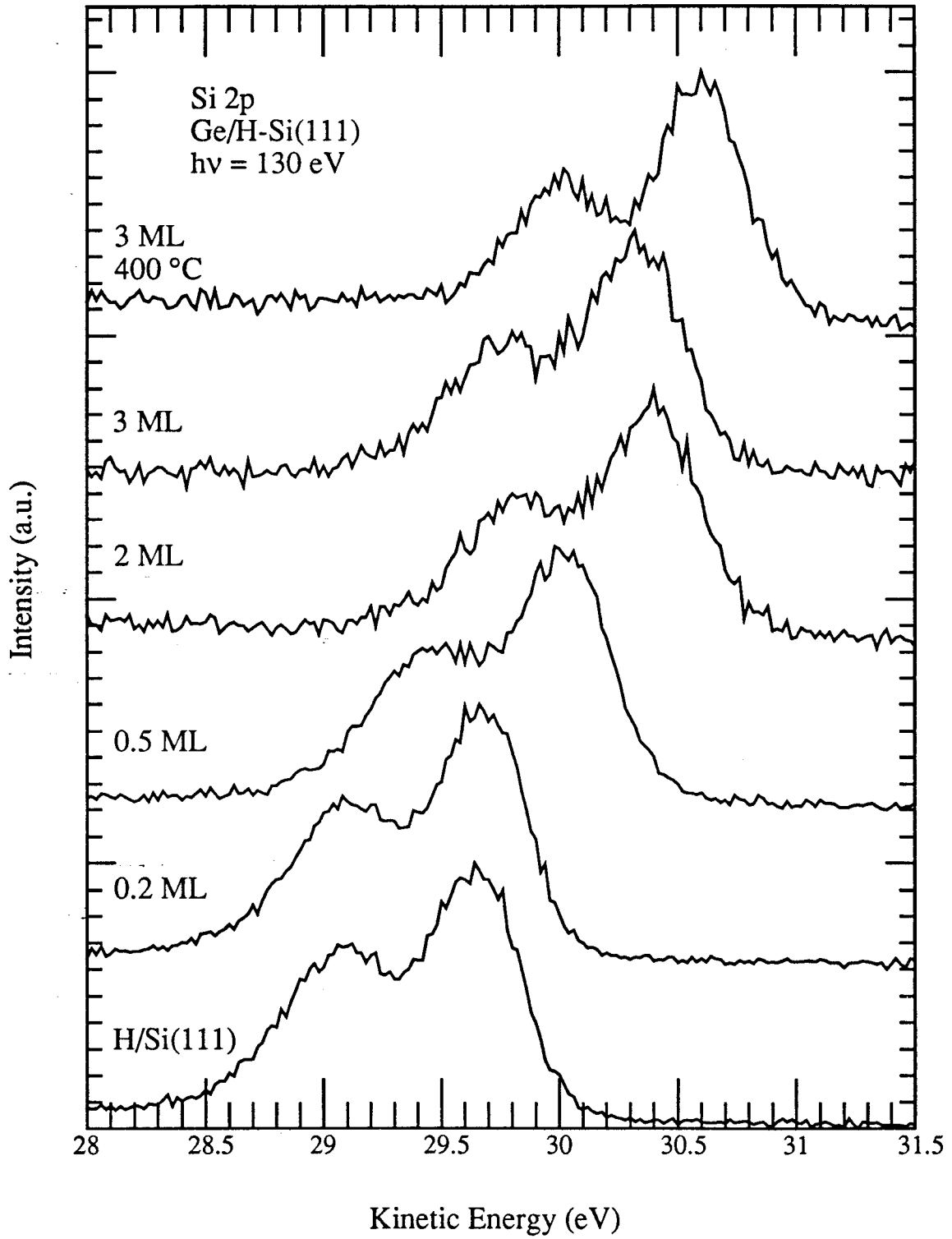


Figure 3: Si 2p core level spectra ( $h\nu = 130$  eV) with different Ge coverages are shown.

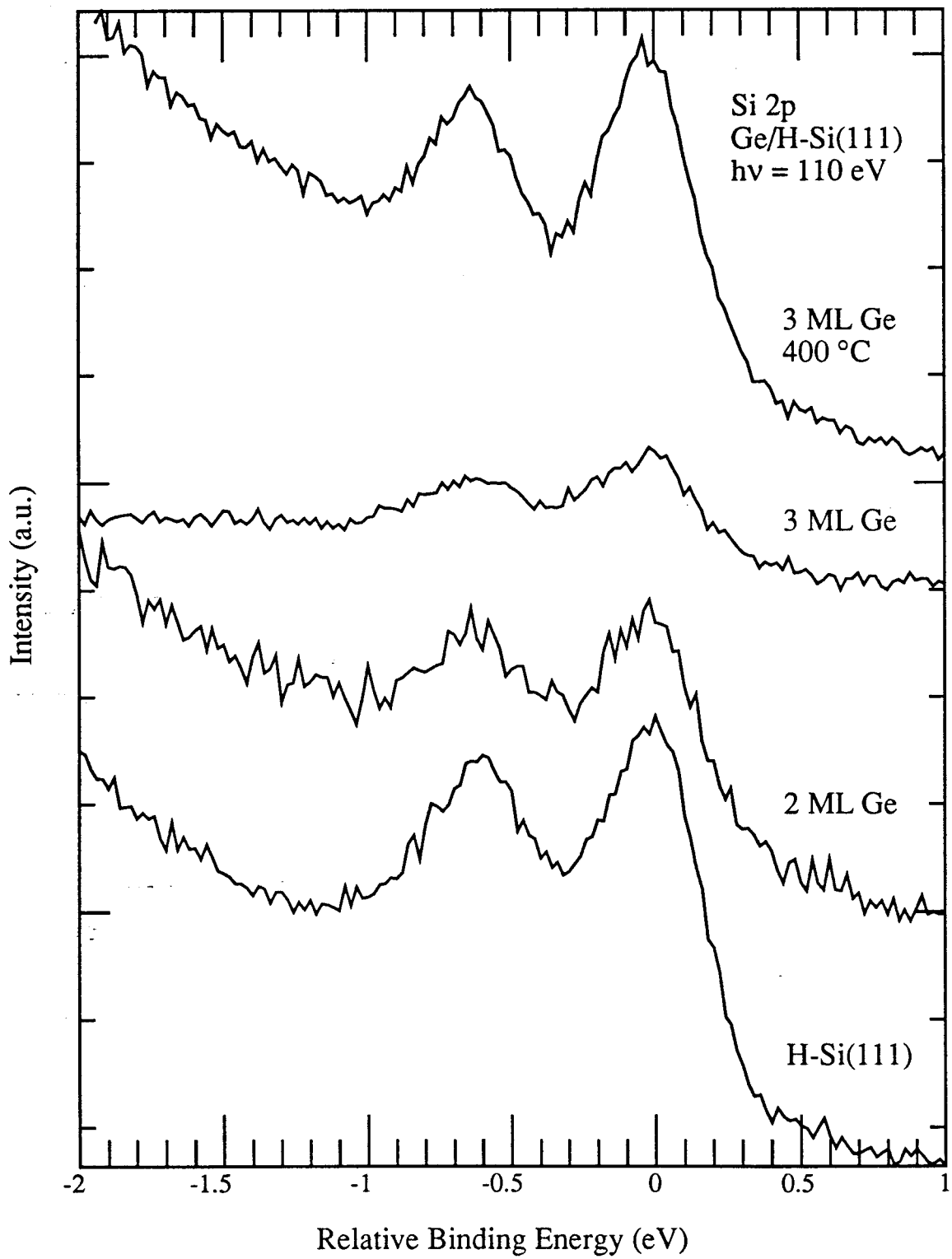


Figure 4: Si 2p core level spectra ( $h\nu = 110$  eV) with different Ge coverages are shown.

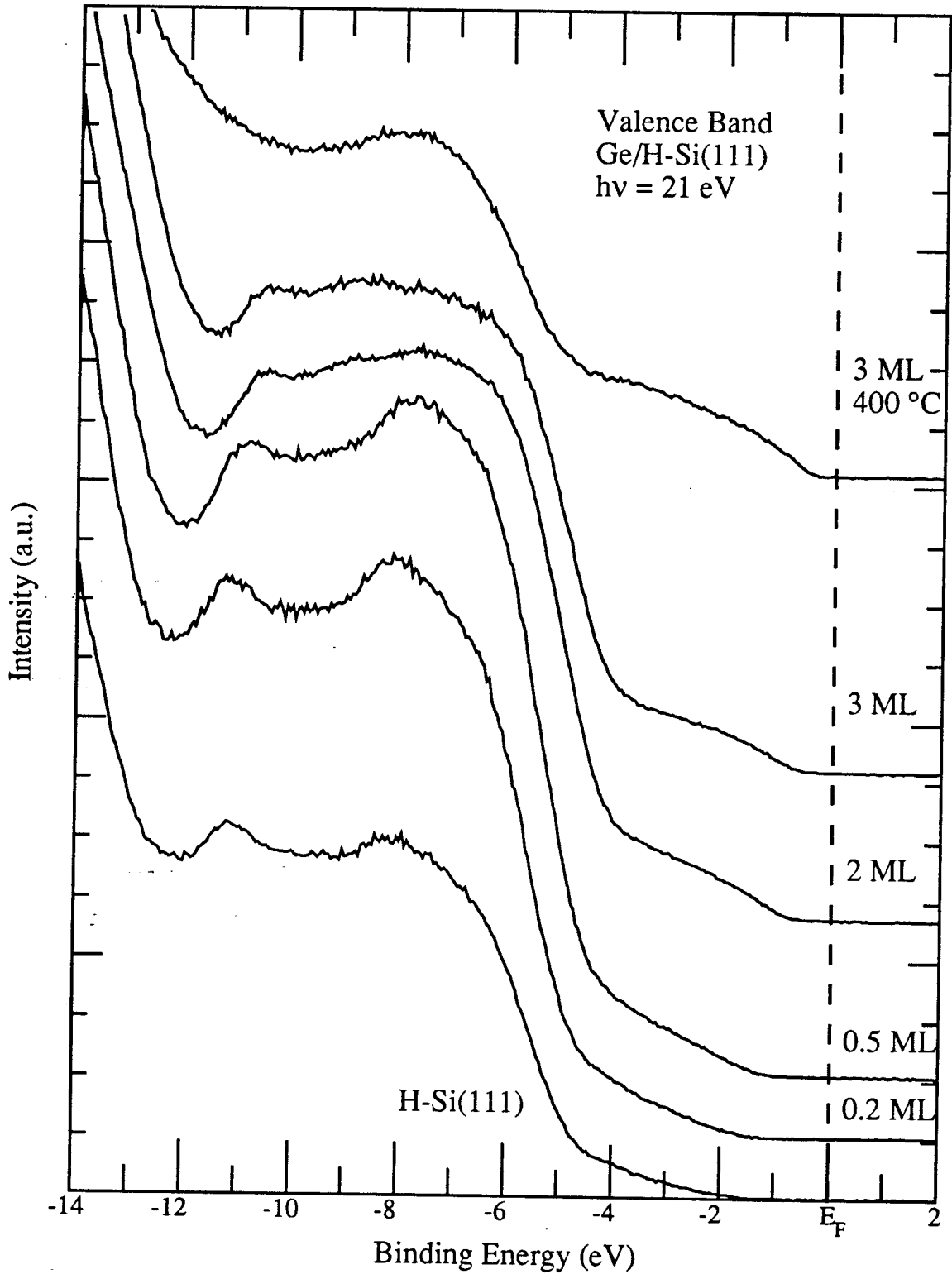


Figure 5: Valence band spectra ( $h\nu = 21 \text{ eV}$ ,  $\Theta = 0$ ) with different Ge coverages are shown.