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HREELS of HN₃ and DN₃ on Si(110)

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Temperature Dependence of the UPS and
HREELS of HN_3 and DN_3 on Si (110)

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Abstract

HN₃ was used for the first time as a nitrogen source for nitridation of Si surfaces. Its interaction with Si(110) was studied with HREELS and UPS at temperatures between 120 and 1350 K. HN₃ was found to adsorb molecularly on the Si surface at 120 K, as all molecular vibrational peaks, such as HN-NN stretching at 150 meV, HNN=N stretching at 265 meV and H-NNN stretching at 414 meV, were clearly observed in HREEL spectra. A similar HREELS study of DN₃ was carried out to confirm some of the EELS assignments. Upon warming up to 220 K, HN₃ started to dissociate into N₂ and NH, which further dissociated to give N and H as the surface was annealed from 580 to 800 K. H adatoms were observed to desorb at T > 800 K, while N remained on the surface, forming Si₃N₄ at T≅1350 K.

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Introduction

Nitridation of semiconductor surfaces, particularly that of silicon¹⁻³ is an important microelectronic fabrication process. It is also relevant to the preparation of Group III - metal nitrides⁴⁻⁶, such as GaN and InN; they are potential high band-gap semiconductors.

Different groups have conducted various investigations on the interaction of nitrogen-containing species with silicon single crystal surfaces; these include NH₃ on Si(111)⁷⁻⁹, N₂ on Si(111)¹⁰, N on Si(111)^{11,12}, NO on Si(111)¹³, and NH₃ on Si(100)^{14,15}, just to mention a few examples. Most of these studies have shown that in the temperature range between 600 and 800 K, a planar or deformed planar structure of Si₃N was formed on the surface. At higher temperatures (>1300 K), the Si₃N structure converted into Si₃N₄ on the silicon surface.

In our continuing search for more facile and clean N-sources, we have recently studied the adsorption of hydrazoic acid (HN₃) on a Si(110) single crystal surface. We have used HREELS and UPS techniques for surface species diagnostics. DN₃ was also used to confirm some of the HN₃ HREELS peak assignments. The result of this studies, including that of temperature-dependence measurements, is presented in this report.

Experimental

The experiment was performed in a multi-diagnostic UHV system (base pressure of 4×10^{-11} torr) which has been described elsewhere¹⁶. The modification made for the present study was to utilize the cooling ability of HREELS rod to achieve low temperature spectroscopic measurements down to 120 K. Reagent gas was dosed directly onto the surface through a 1/8 inch stainless steel tube, which was about 2 cm away from the silicon sample.

In HREELS studies, an electron beam with the primary energy of $E_p = 5$ eV and the resolution of $\Delta E(\text{FWHM}) = 10$ meV in the straight through mode was used. Angular dependence measurements were made possible by turning the movable energy analyzer around the axis perpendicular to the incident plane of the electron beam.

UPS measurements were carried out in a different compartment of the UHV chamber. The photoelectron spectra were obtained with a He II (40.8 eV) source. The reference energy point $E_F = 0$ to be shown in figure 4 was calibrated with the UPS peaks of the S_1 , S_2 , S_3 surface states of a clean Si(111) surface¹⁷.

Si(110) samples from Virginia Semiconductor Co. were cut into 1.5×1.0 cm²; the samples were cleaned by flash-heating to >1470 K until no obvious carbon loss peak could be observed in HREELS and samples showed a 4×5 LEED pattern. Below 300 K, surface temperature was monitored with a Pt-chrome thermocouple inserted between the sample and its holder. Between 500 and 925 K, sample temperature was determined by measuring its resistance. The temperature-resistance curve obtained at $T > 925$ K could be

calibrated with a pyrometer, which was used to measure the temperature higher than 925 K.

$\text{HN}_3(\text{DN}_3)$ was synthesized in a vacuum sample preparation system. Dried NaN_3 (Aldrich Co.) was placed in a 100 ml 3-neck round bottom flask which was connected in series to 2 cold traps (195 and 77 K). After thorough pumping and degassing, the NaN_3 sample was then slowly mixed with H_3PO_4 (or D_3PO_4) (Aldrich Co.) through an evacuable funnel. HN_3 (or DN_3) produced was evacuated through the 195 K trap (to remove water) and condensed entirely without loss at the 77 K cold trap. Further purification of the 77 K condensate was made by distilling it from 180 to 77 K. FTIR analysis of the prepared HN_3 sample showed no detectable impurities and that of DN_3 indicated a D-atom enrichment of about 95%.

Results and Discussion

A. HREEL Spectra of HN_3

Figure 1 shows HREEL spectra of HN_3 on Si(110) at different temperatures obtained under specular mode. The surface was dosed with 0.3 L of HN_3 at 130 K and then annealed for 2 minutes to reach the indicated surface temperature; all spectra were taken after the surface was cooled down to 130 K. At 130 K, loss peaks at 55, 77, 150, 160, 265, and 414 meV were observed; these peaks compare favorably with gas phase HN_3 IR and/or Raman spectra as shown in Table 1.

Upon warming up to 220 K, the 55, 77 and 150 meV peaks, due to N₃ deformation and N-N₂ stretching respectively, almost disappeared, while a shoulder at 90 meV due to SiN_x stretching, started to grow and the peak at 414 meV (H-N₃) shifted to 430 meV, which is believed to be resulted from HN stretching vibration⁸.

When the surface was annealed from 580 to 800 K, the loss peak around 100 meV, corresponding to the Si_xN (x=1,2,3) mode¹⁸⁻²⁰ became broader; its unsymmetrical shape may be due to the different bond formation between Si and N as observed by Edamoto and other others¹⁸⁻²⁰. The 265 meV loss peak due to N=N stretching shrank and a new peak at 256 meV, corresponding to the well known Si-H stretching vibration²¹ started to grow. The intensity of the 430 meV peak decreased concomitantly, reflecting a substantial dissociation of the HN species, the source of the H atom for Si-H formation.

After annealing at 1350 K, very strong peaks at 65, 93, and 130 meV appeared, because of the formation of silicon nitride(Si₃N₄). This result is consistent with Taguchi's observation in conjunction with the nitridation of Si(100)²² and Si(111)¹⁸ surfaces. They reported that annealing at 1350 K yielded the loss peaks at 60, 90, 109 and 130 meV for Si(100) and 60, 90, and 120 meV for Si(111). In both cases, Si₃N₄ was believed to be formed. The 2 humps around 223 and 260 meV peaks observed in our studies are likely the combination of 93 and 130 meV peaks and the overtone of the 130 meV peak, respectively, as shown by the inset of Fig. 1.

In summary, at 130 K HN₃ molecularly adsorbed on the Si(110) surface as all the molecular vibration frequencies were clearly observed in the HREELS. When the surface was warmed up to 220 K, HN₃ dissociated into N₂ and HN as

indicated by the disappearance of the HN-N₂ stretching vibration peak at 145 meV and of the two N₃ bending peaks at 55 and 77 meV, respectively, and by the shift of the H-N₃ stretching vibration peak at 414 meV to the H-N stretching vibration peak at 430 meV. According to Heckingbottom's LEED study of N₂ on Si(111)¹⁰ that N₂ molecules do not adsorb strongly on the Si(111) surface at room temperature, we believe that N₂ desorbs readily from the (110) surface after it is formed from the dissociation of HN₃; however, we cannot completely rule out the possibility of N₂ further dissociate to give 2N on the surface in the present studies. In fact, our preliminary XPS study of Si(111)-(7x7) (exposed with HN₃) showed no obvious attenuation of N signal upon annealing the surface to higher temperatures. Annealing the surface from 580 to 800 K causes further dissociation of HN as indicated by the decrease of the 430 meV peak intensity and the appearance Si-H peak at 256 meV. When the Si(110) surface was further annealed at 1350 K, Si₃N₄ was formed at the surface.

B. HREELs of DN₃ on Si(110)

Figure 2 shows the HREELS results of DN₃ dosed at 0.6 L on the Si(110) surface at 120 K. The 128 (DN bend), 158 (DN-N₂) and 270 (DNN=N), 307 (D-N₃) meV bands were clearly observed, which confirmed the peak assignments of the HN₃ HREEL spectra.

It should be pointed out that because of the fast hydrogen-deuterium exchange on the walls of the chamber and inlet line, the corresponding HN₃ peaks also appeared in the spectra; it was found to be difficult to remove these HN₃ peaks completely. Upon heating the surface to various temperatures, essentially the same results as HN₃ on Si(110) surface were observed.

C. Angular dependence study of HN_3 HREELS

Figure 3 shows the angular dependence of the HREEL peaks for the intensities at 150, 270 and 413 meV of HN_3 on Si(110); they are plotted in logarithmic scale vs the off-specular angle (in degrees). For the angular dependence study, other loss peaks were not measured because of their low peak intensities. The very weak angular dependence of the loss peak intensities of those measured peaks implies the lack of dipole absorption, which in turn suggests that the HN_3 molecules are absorbed nearly parallel to the surface.

D. UPS of $\text{HN}_3/\text{Si}(110)$

The temperature dependence of the UPS of HN_3 on Si(110) is displayed in figure 4. When the Si(110) surface was dosed with 0.3 L of HN_3 at 120 K, the Si 3p valence states at about 3.0 eV were significantly attenuated and three main features around 7.1, 9.2, and 13.3 eV were observed as shown in fig.4a. The gas phase UPS (He I) of HN_3 measured by Dyke et al.²³, also showed three peaks with the energy separations of 1.5 and 3.3 eV, respectively; this observation agrees reasonably with ours, 1.1 and 4.1 eV. When the surface was warmed up to 250 K, the 7.1 eV peak shifted to 6.4 eV and the 13.3 eV band vanished almost completely, while a shoulder centered around 11.5 eV was present. The energy separation of 5.1 eV between the two peaks agrees very well with Karcher's UPS results²⁴ for a-SiN:H=1 film, which showed an energy separation of 5.1 eV and also with Kubler's work for NH_x on Si(111)⁹, where the energy separation was observed to vary from 5.25 to 5.7 eV.

When the surface was heated to 830 K, the 6.5 eV peak shifted back to 7.5 eV and the 11.5 eV was reduced to a small hump around 12.4 eV. The 7.5 eV feature is due to N $2P_{xy}$ in Si_3N_4 as was observed by Karcher et al.²⁴ The Si valence states peaking around 3.0 eV were gradually reestablished as the annealing temperature was increased, indicating that the partial desorption of HN_3 and its cracked species, such as H and N_2 , occurs at this temperature (830 K).

At even higher temperatures, $T_s \geq 1200$ K, the UPS result is similar to that of a clean Si(110) surface; however, the intensity ratio of the peaks at 7.5 and 3.0 eV are bigger for the annealed surface than the clean surface, which indicates some N atoms might still be left on the surface. The HREELS study has also shown that even at 1350 K there are still some nitrogen left on the surface as Si_3N_4 . A similar UPS study of HN_3 on Si(111) surface currently under way shows a much stronger N $2P_{xy}$ band at around 7.5 eV, when the surface was annealed at 1350 K. These new results will be reported elsewhere. When the surface was flash-heated at 1520 K, a clean Si(110) surface was reestablished.

Conclusion

In this work HN_3 was used for first time as a nitrogen source for the nitridation of silicon surfaces. Its interaction with a Si(110) surface was studied with HREELS and UPS in the temperature range from 120 to 1350 K, using both HN_3 and DN_3 .

HN_3 was found to molecularly adsorbed on the surface at 120 K and it began to dissociate into the HN radical and N_2 at about 220 K. The HN species further dissociated to give H and N atoms when the surface was annealed at

higher temperatures. The H atom was found to desorb at temperatures higher than 800 K, whereas the N atom remained on the surface up to 1350 K, at which both UPS and HREELS showed that silicon nitride in the form of Si₃N₄ was produced.

Acknowledgment

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Table 1. Vibrational frequencies (in meV) and assignments for HN₃ and DN₃ observed in the gas phase and on Si(110).

Mode		HN ₃ (g)*	HN ₃ (ads)	DN ₃ (g)*	DN ₃ (ads)
Assignment					
δ	(N ₃)	66	55	61	
δ	(N ₃)	75	77	73	73
ν	(HN-N ₂) or DN-N ₂	143	150	147	158
ν	(H-N) or D-N	157	160	118	128
ν	(HN ₂ =N) or DN ₂ =N	265	265	262	270
ν	(N-H) or D-N ₃	414	414	307	307

*Ref. 25

Captions:

- Figure 1. HREEL spectra of (a) clean, (b) - (f) HN_3 exposed Si(110) surface at 120 K and after heating to various temperatures then cooling to 120 K. The initial exposure was 0.3 L ($1\text{L} = 1 \times 10^{-6}$ Torr S). Top right was the Zoom-in HREELS after heating to 1350 K.
- Figure 2. HREEL spectra of (a) clean, (b)-(e) DN_3 exposed Si(110) surface at 120 K and after heating to various temperatures then cooling to 120 K. The initial exposure was 0.6 L. The top right was the zoom-in HREELS after heating to 1350 K.
- Figure 3. Angular dependence EELS of 0.3 L HN_3 exposed on the Si(110) surface. The EELS signal intensities (peak height) were measured at the off-specular angle.
- Figure 4. He (II) (40.8 eV) photoelectron spectra of (a) clean, (b)-(e) 0.3 L HN_3 exposed Si(110) surface at 120 K and after heating to various temperatures then cooling to 120 K.

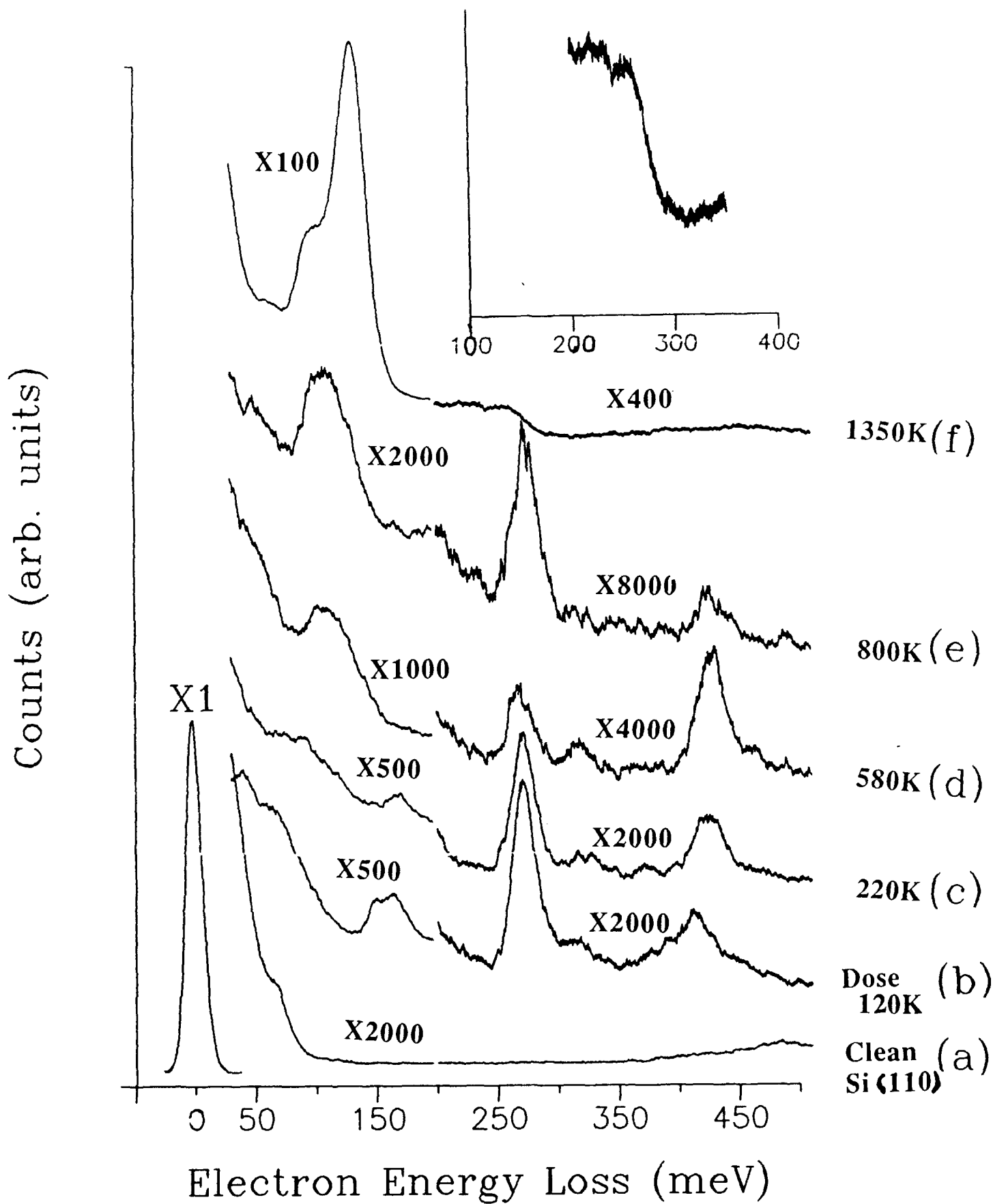


Figure 1

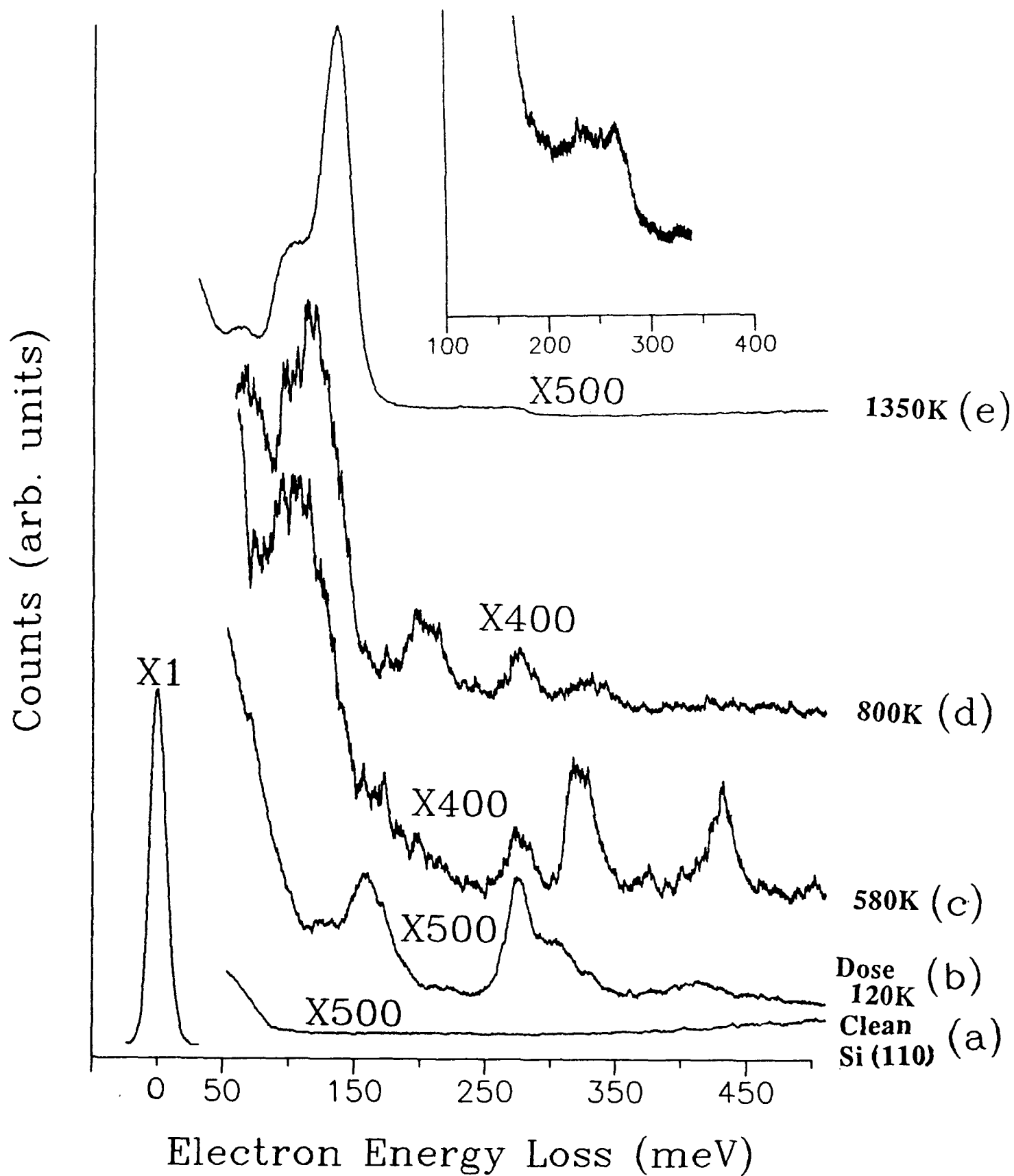


Figure 2

AREELS of HN3/Si(110)

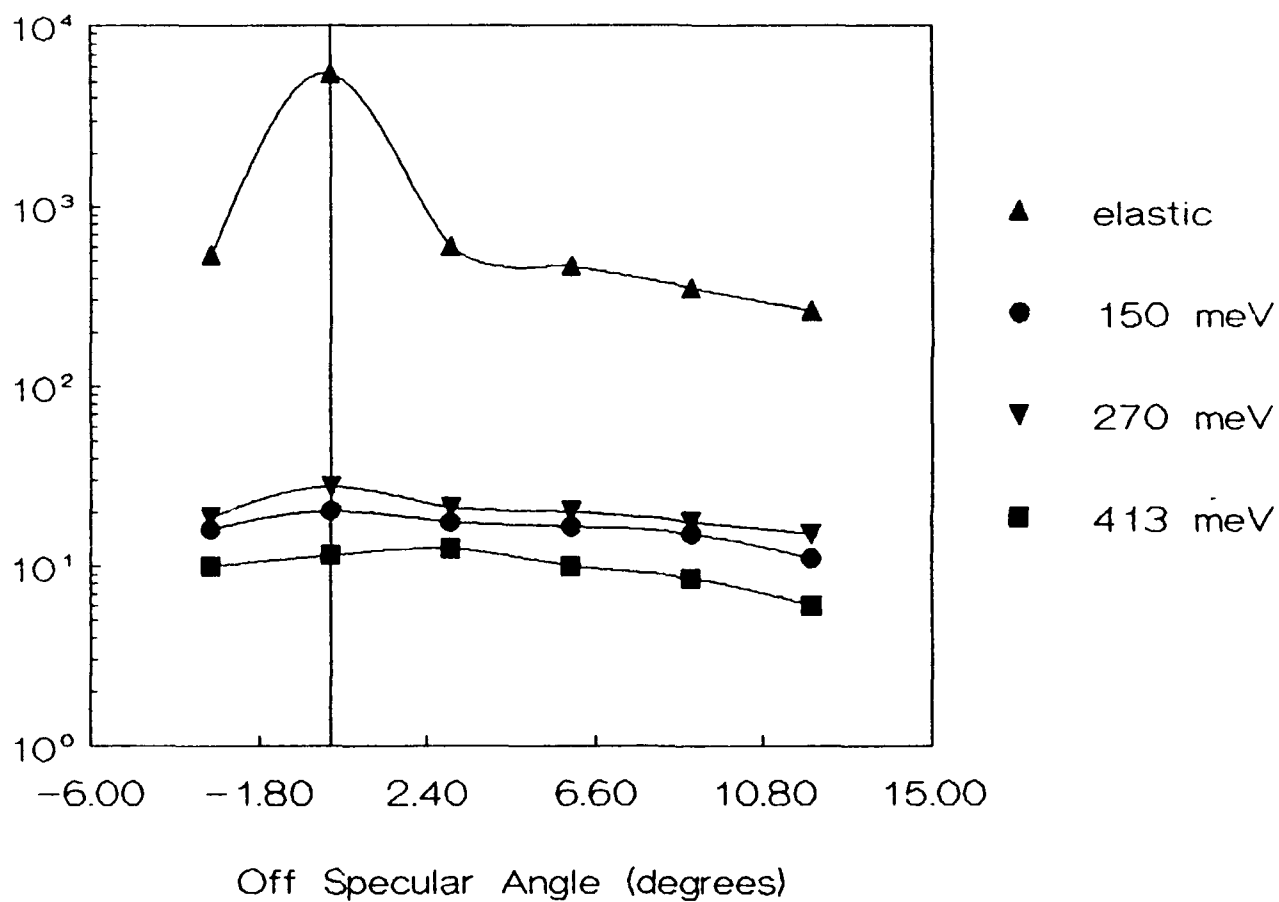


Figure 3

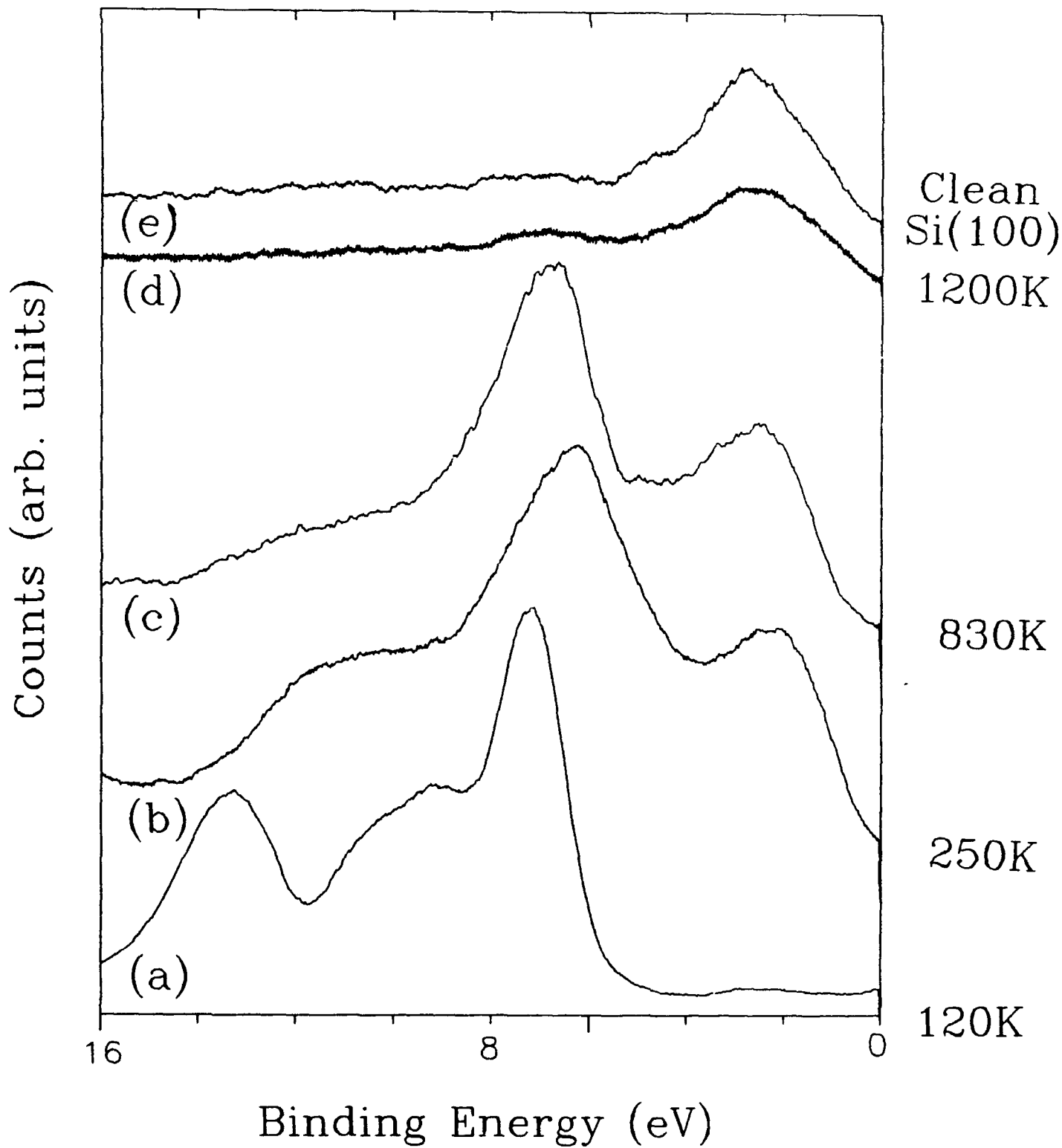


Figure 4