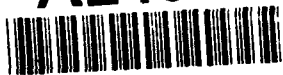


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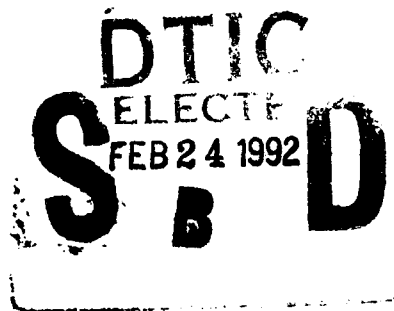
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Adsorption and Decomposition of Trimethyl Indium
on Si(111)-7x7 Studied with XPS, UPS and HREELS

by

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Abstract

The techniques of XPS, UPS and HREELS are utilized to investigate the thermal decomposition of trimethyl indium (TMIn) on Si(111)-7x7. When dosed at 120 K, TMIn was primarily molecularly adsorbed on the surface with a minor splitting of CH₃ groups from the central In atom. Upon annealing the sample at 280 K, partial desorption of TMIn was accompanied by further dissociation of the In-C bonds; Annealing the surface from 540 to 620 K caused complete cracking of In-C bonds, simultaneously a new peak at 128 meV was observed in HREELS, which is assigned to the CH₃ groups attached to the surface. At 620 K and above, the Si-H species was evident in both UPS and HREELS, indicating the onset of C-H bond cracking; meanwhile the atomic In started to desorb. These processes continued as the sample was further annealed up to 790 K. Finally at T>950 K, SiC was formed after the complete cracking of C-H bonds and the desorption of In and H species.



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Introduction

There has been a rapidly growing interest in OMCVD of III-V compound semiconductors because of its fundamental and technological importance, including the application in optoelectronic and microwave devices¹. From the fundamental studies of adsorption and decomposition of organometallic compounds on different substrates, information about the decomposition mechanism and reaction dynamics, if coupled with molecular beam and laser techniques, can be obtained. These basic mechanistic data will invariably lead to a better understanding and improvement of industrial processes.

Recently, a number of related studies on organometallic reactions on various single crystal surfaces have been carried out. For example, trimethyl aluminum (TMAI) on Si(100)², TMAI on Ru(001)³, trimethyl gallium (TMGa) on Si(100)⁴, and Si(111)⁵, triethyl gallium (TEGa) on Si(100)⁶, TMGa and TEGa on GaAs⁷, tetramethyl germanium on Si(100)⁸ and more recently TMGa on Pt(111)⁹. On the other hand, very little is known about the reaction of trimethyl indium (TMIn) on well characterized surfaces. There have been numerous studies of TMIn decomposition reactions in the gas phase¹⁰⁻¹⁷, however.

Experimental

The experiments were carried out in a custom-designed UHV system (Leybold) equipped with HREELS, XPS, UPS, LEED and AES as described elsewhere.^{18,19} Si(111) single crystal was cut from a 2" wafer (10 Ω -cm, Virginia Semiconductor) into 1.5 x 1.0 cm² samples. The crystal was then cleaned chemically with ~5% HF solution and annealed at > 1500 K in the UHV chamber. Si(111) surface cleaned in this way

produced a sharp 7x7 LEED pattern and no impurities (N, O, C) could be detected by AES and/or XPS. HREEL spectra also showed an essentially clean surface.

TMIn (electronic grade) from Morton Thiokol Inc. was further purified by pumping the sample at dry ice temperature for a few hours and then introduced onto the surface by back filling the chamber to 1×10^{-8} torr. The approximate dosage was estimated on the basis of the ion gauge reading without calibration for the different gases.

Results and Discussion

XPS

Figures (1a) and (1b) show a series of C_{1s} and $In_{3d,5/2}$ XPS spectra, respectively, taken by dosing ~6L TMIn on Si(111)-7x7 at 120 K and then annealed to the indicated temperatures. When dosed at 120 K, peaks at 283.7 and 444.1 eV were observed for C_{1s} and $In_{3d,5/2}$ photoelectrons respectively. Upon annealing to 610 K, intensity attenuations with minor peak shifts to higher binding energies for both C and In peaks were noted. The change is mainly due to the desorption of some TMIn, C-containing species and the decomposition of the In-C bonds.

Further annealing of the sample to higher temperatures caused a continuous shift of C_{1s} peak, but to lower B. E. because of the cracking of the C-H bonds. At 940 K a peak at 282.8 eV was observed. The value is in very good agreement with that of 282.9 eV taken from a SiC sample,²⁰ indicating the formation of SiC at 940 K following the cracking of In-C, C-H bonds and the desorption of In, H and possibly some partial C- containing species.

In_{3d} XPS spectra showed a similar trend as that of C_{1s} spectra upon the annealing, except that at $T > 600$ K, its peak intensity decreased quickly and essentially vanished at 940 K, due to the desorption of In species.

Figure 2 shows the variation of C_{1s} and In_{3d} signal intensities (peak area) with temperature as the surface was annealed up to 940 K. At ~280 K, both C and In signals decreased while their ratio remained essentially the same, which indicates the partial desorption of TMIIn molecules. On the other hand, between 280 and 540 K, the C_{1s} intensity continued to drop, but the In intensity remains the same. This obviously suggests the cracking of the In-C bonds and the desorption of some C-containing species, e.g. CH_3 , CH_4 and C_2H_4 etc. Unfortunately thermal desorption study could not be carried out with the present system. However in an earlier study¹⁹, CH_3 radicals were detected selectively by the resonance enhanced multiphoton ionization technique, when TMIIn was continuously introduced onto a Si(111) surface above 500 K. Further annealing at 590 K caused the attenuation of both C_{1s} and In_{3d} peak intensities, which should be due to the desorption of incompletely dissociated species $In(CH_3)_x$ ($x < 3$) or In-and C-containing species individually. In a TPD study of TMGa on Si(111) surface⁵, species of $Ga(CH_3)_3$, $GaCH_3$, CH_3 , CH_4 , C_2H_4 and Ga were found to desorb from the surface in a temperature range of 300 - 920K. Above 600 K, C_{1s} signal remained unchanged, while In_{3d} signal continued to decrease due to the desorption of the In species. This is consistent with a TPD study of In/Si(100)²¹, where a single peak at ~900 K and two peaks at ~800 and ~900 K were observed for low and high In coverages, respectively.

UPS

Figure 3 shows a series of UPS spectra taken by dosing ~1L TMIIn on Si(111)-7x7 and then annealing at the indicated temperatures. When dosed at 120 K, peaks at 8.4, 16.7, 19.5 and 20.4 eV below E_F were clearly evident. These peaks were assigned to σ_{C-H} , C_{2s} and $In_{4d} 5/2, 3/2$ molecular orbitals, respectively, by analogy to the gaseous TMIIn UPS spectra^{22,23}, which are also shown in Fig. 3. The peak due to In-C orbital,

expected at ~ 4.4 eV below E_F according to the gas phase result, was not well separated from the Si valence band. However the peak at 4.0 eV can be very clearly seen in the difference spectra between the dosed sample and the clean surface (as given by the dashed curves), in which the large contribution from the Si valence band was eliminated. The existence of this In-C peak, consistent with our HREELS results as will be discussed later, indicates the presence of the molecularly adsorbed of TMIn at 120 K. On the other hand, the deviation of binding energies for both C-H and In-C from the gas phase values may suggest a distortion and a possible slight dissociation of the molecules upon adsorption. In fact, the broad peak at 8.4 eV may have some contributions from the Si-C bond, which is expected at the lower binding energy side of the C-H peak, due to the CH_3 groups attached to the surface.

The C_{2s} peak at 16.7 eV was not reported in the gaseous TMIn spectra, but was observed at 16.2 and 17.0 eV in the case of $\text{CH}_3\text{N}_2\text{H}_3$ ¹⁸ and CH_3F ²⁴ on Si(111) respectively. The $\text{In}_{4d,3/2}$ peak at 20.4 eV may have a little contribution from the Si surface state, S_2 , excited by He I photons. Note that the S_2 surface state was substantially suppressed upon the adsorption of 1L TMIn as shown in the corresponding He II spectra, especially in the difference spectra where a negative peak at 0.8 eV below E_F was clearly evidenced.

When the sample was annealed at ~ 280 K, there was little change in the peak positions, however peak intensity attenuation was noticeable, especially the In-C peak at 4.0 eV in the difference spectra. This attenuation should reflect the desorption of some TMIn and a further split off of CH_3 groups from the central In atom. The 4.0 eV peak was significantly reduced as the sample was annealed at 540 K, and totally vanished at higher annealing temperatures.

Further annealing the surface at 620 K caused the growing of a shoulder at ~ 5.4 eV due to the Si-H bond, which became a little stronger at 730 K; however, it was still not well resolved from the much more intense C-H and Si-C peaks now shifted to

7.9 eV. The HREELS result to be discussed later also showed a Si-H band in this temperature range. Meanwhile the C-H peak showed a less significant change except the continuous shift to the low binding energy side, and at 950 K, a peak at ~7.5 eV indicates the formation of SiC following the cracking of the In-C and C-H bonds.

In addition, In(4d) signals also showed some interesting changes. First the peak shifted ~0.5 eV towards the lower B.E. energy side at 540 K and then continued to shift to give peaks at 18.8 and 19.7 eV for In_{4d, 5/2} and In_{4d, 3/2} respectively at 620 K. The d-electron peak shifting toward lower B. E., although less significant, was also observed in the gaseous DMCD UPS spectra, when two CH₃ groups were released from the central Cd atom, and was confirmed by ab initio calculations.²² Thus In peak shift here should also reflect the cracking of the In-C bonds and fully support the other observation of the In-C peak intensity decreasing in the same temperature range. At 620 K, the intensities of the In peaks were enhanced somewhat; the origin of this enhancement is not clear. However, it is likely that the enhancement may result from the complete separation of In-(CH₃)_x as well as the desorption of some C-containing species, therefore In 4d electrons were less shielded from the photons and the emitted photoelectrons were less attenuated. Further annealing the sample at higher temperatures caused In peaks to decrease continuously and totally disappear at 950 K due to desorption. Finally, it should be pointed out that S₂ surface states of Si were not recovered until the surface was annealed at much higher temperatures to remove C species.

HREELS

A series of HREELS spectra shown in Fig. 4 illustrates the annealing effect on a 1L TMIn dosed Si(111)-7x7 surface. When the surface was dosed at 120 K, peaks at 61, 90, 110 (shoulder), 148, 180 and 366 meV appeared. By analogy to IR/Raman

spectra of the gas phase $\text{TMIn}^{25,26}$, peaks at 61, 90, 148 and 366 meV can be easily assigned to In-C stretching, CH_3 rocking, CH_3 symmetric deformation and CH_3 symmetric and antisymmetric stretching vibrations, respectively, as shown in Table 1. The peak at 180 meV due to CH_3 antisymmetric deformation vibration could be clearly observed in TMB (trimethyl boron), but much weaker in TMGa and inactive in TMIn IR/Raman spectra.²⁵ It was also observed as a fairly strong peak in HREELS spectra of TMAI and TMGa dosed Si, Ru and Pt surfaces^{2-6,9}. Here a peak at 180 meV may suggest the distorted adsorption of TMIn on Si(111)-7x7 or may be due to a slight dissociation of the TMIn molecule. This would also explain the weak yet noticeable peak at 110 meV due to the rocking vibration of CH_3 attached to a partially dissociated or distorted molecules. The partial dissociation of TMGa on Si(111) at 300 K⁵ and on Si(100) and Pt(111) at 120 K⁹ has been reported. It should be noted that the Ga-C bond is stronger than that of In-C.

When the 1L TMIn dosed sample was annealed at 280 K, the attenuation of all peaks was noticed, especially the peak corresponding to the In-C stretch at 61 meV. This suggests that both the desorption of TMIn and further split off of the CH_3 groups occur at this temperature. This argument is supported by the result of further annealing at higher temperatures. At 540 K, the In-C peak at 61 meV essentially vanished, meanwhile the peak at 90 meV was broadened and shifted to ~98 meV, which derives mainly from the Si-C stretching and CH_3 rocking vibrations. In addition, a new peak at ~128 meV appeared and grew a little at 620 K. To assign this peak unambiguously is difficult because its origin may be CH_2 , CH_3 or C_2H_4 etc. The latter two were detected as desorbing species in a TPD study of TMGa on Si(111)⁵, although not on Si(100).⁴

Lee et al.⁴ observed a peak at 900 cm^{-1} (112 meV) and shifted to 960 cm^{-1} (119 meV), when a TMGa dosed Si(100) sample was annealed at 450 K and 750 K respectively. Simultaneously, a peak at 1420 cm^{-1} (188 meV) was also observed.

Both peaks were assigned to the CH₂ group attached to the surface. However in the present study, 188 meV peak would be very weak, if it existed at all. TMGa on Si(111) also showed the growing of a shoulder at ~120 meV when the surface was annealed at 450 ~ 700 K⁵, where CH₃ groups were believed to split from TMGa onto the surface because of the disappearance of the Ga-C stretching peak at 67 meV.

In the studies of C₂H₄ on Si(100) and (111) surfaces, Yoshinobu et al.^{27,28} observed peaks at 112 and 117 meV, respectively, which were assigned to the rocking vibration of CH₂ groups by analogy to the model molecule, C₂H₄Br₂. On the other hand, IR/Raman spectra of CH₃Br also showed a peak at ~118 meV due to the CH₃ rocking vibration. The C-C stretching vibration at 136 and 135 meV for ethylene adsorbed on Si(100) and (111), respectively, could be another possible candidate for the 128 meV peak observed in the present study; however this bond is unstable at 650 K on Si(100) and was not reported on Si(111). Thus the C-C stretching vibration is unlikely to be responsible for the 128 meV peak, which was only gradually shifted to 125 meV upon annealing the sample up to 790 K.

Based on the above discussion and the lack of information on isolated CH_x groups on Si substrates and the desorbed species from TMI_n on Si(111), we tentatively assigned the 128 meV peak to the rocking vibration of the CH₃ group attached to the surface. We may rule out the possibility of the presence of the CH₂ species, which could be produced by the direct dissociation reaction, CH₃ (a) → H(a) + CH₂ (a), since there was no Si-H peak being observed at this temperature yet. Further study will be carried out in the near future, on the spectroscopy of CH_x species using molecules which can produce the CH_x species more readily and clearly.

Annealing the sample at 620 K caused the 98 meV peak broadened further. This broad peak may have contributions from Si-C stretch, CH₃ rock and CH₂ rock or twist vibrations. The possibility of the presence of CH₂ at 620 K is suggested by the appearance of the weak Si-H stretch vibration at 257 meV, the red shift of the peak at

180 to 176 meV and the broadening of the CH₃ stretch vibration at 368 meV. In the study of C₂H₄ on Si(111)²⁸ mentioned above, peaks at 176 and 363 meV were observed for CH₂ scissor and C-H stretch vibrations, respectively.

The continuous annealing of the sample at 690 K caused further cracking of C-H bonds, as evidenced by the growing of the Si-H vibration, the attenuation of the peak at 176 meV and the shifting of the peaks from 127 to 125 meV and 368 to 363 meV respectively. The 176 meV peak was further attenuated and the 260 meV one grew a little stronger as the surface was annealed at 790 K. Finally at 1050 K, only a single peak at 112 meV due to Si-C²⁹ was observed.

Conclusion

TMIn was found to be adsorbed molecularly on a Si(111)-7x7 surface at 120 K with a slight dissociation of the In-C bonds. At 280 K, partial desorption of TMIn was accompanied by a further cracking of the In-C bonds. Annealing the sample at 540-620 K caused the complete breaking of the In-C bonds and further annealing led to the cracking of the C-H bonds. Above 600 K, the In atom started to desorb and finally at T_s > 950 K, only C remained on the surface.

Acknowledgments

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Table 1. IR/Raman spectra of gaseous Ga(CH₃)₃ and In(CH₃)₃ and the HREELS of In(CH₃)₃ on Si(111)-7x7

Mode	Ga(CH ₃) ₃		In(CH ₃) ₃		In(CH ₃) ₃ on Si(111)-7x7 HREELS
	Raman cm ⁻¹ (meV)	IR cm ⁻¹ (meV)	Raman cm ⁻¹ (meV)	IR cm ⁻¹ (meV)	
C-H ₃ str.	2963 (367) 2904 (360)	2990 (371) 2915 (361)	2974 (369) 2910 (361)	3000 (372) 2920 (362)	367 meV
CH ₃ asym. def.	1435 (178)	1435 (178) 1405 (174)			180 meV
CH ₃ sym. def.	1197 (148) 1185 (147)	1206 (150)	1157 (143) 1116 (138)	1155? (143)	148 meV
CH ₃ rock	772 (96) 622 (77)	766 (95)	725 (90) 635 (80)	725 (90) 687 (85)	90 meV
M-C str.	570 (71) 522 (65)	576 (71)	495 (62) 467 (58)	500 (62)	61 meV
M-C def.	164 (20)		132 (16)		

Figure Captions

- Fig.1. C_{1s} (1a) and $In_{3d, 5/2}$ (1b.) XPS spectra taken by dosing $\sim 6L$ $TMIIn$ on $Si(111)-7 \times 7$ at 120 K and then annealing at the indicated temperatures.
- Fig. 2. The variations of C_{1s} (Δ) and $In_{3d, 5/2}$ (O) XPS signal intensity as a $\sim 6L$ $TMIIn/Si(111)$ sample was annealed up to 940 K.
- Fig. 3. UPS spectra taken by dosing $\sim 1L$ $TMIIn$ on $Si(111)-7 \times 7$ at 120 K and then annealing at the indicated temperatures. Dashed lines are the difference spectra between the dosed and annealed sample and the clean surface.
- Fig. 4. HREELS spectra taken at essentially the same conditions as in Fig. 3.

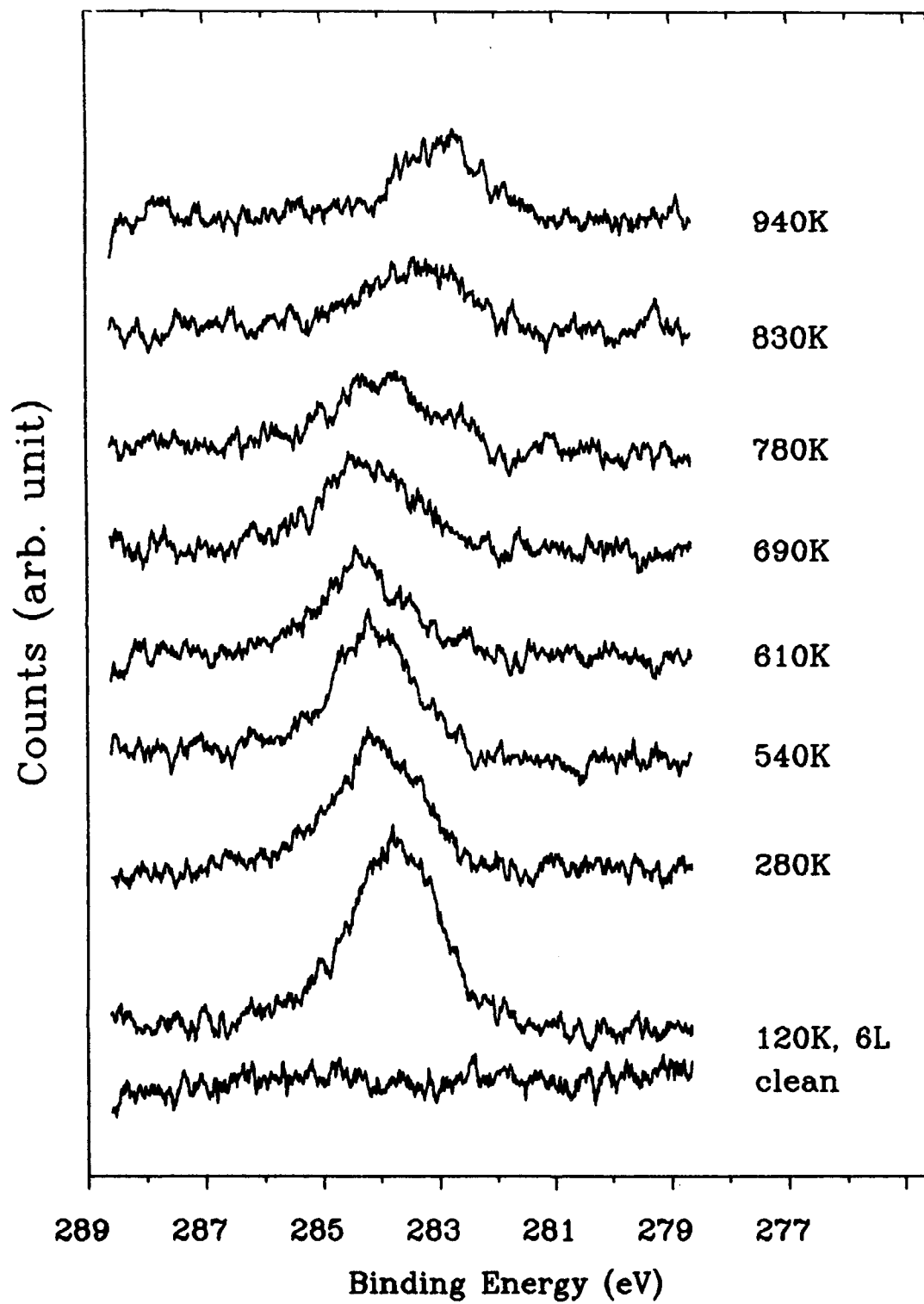


Fig. 1a

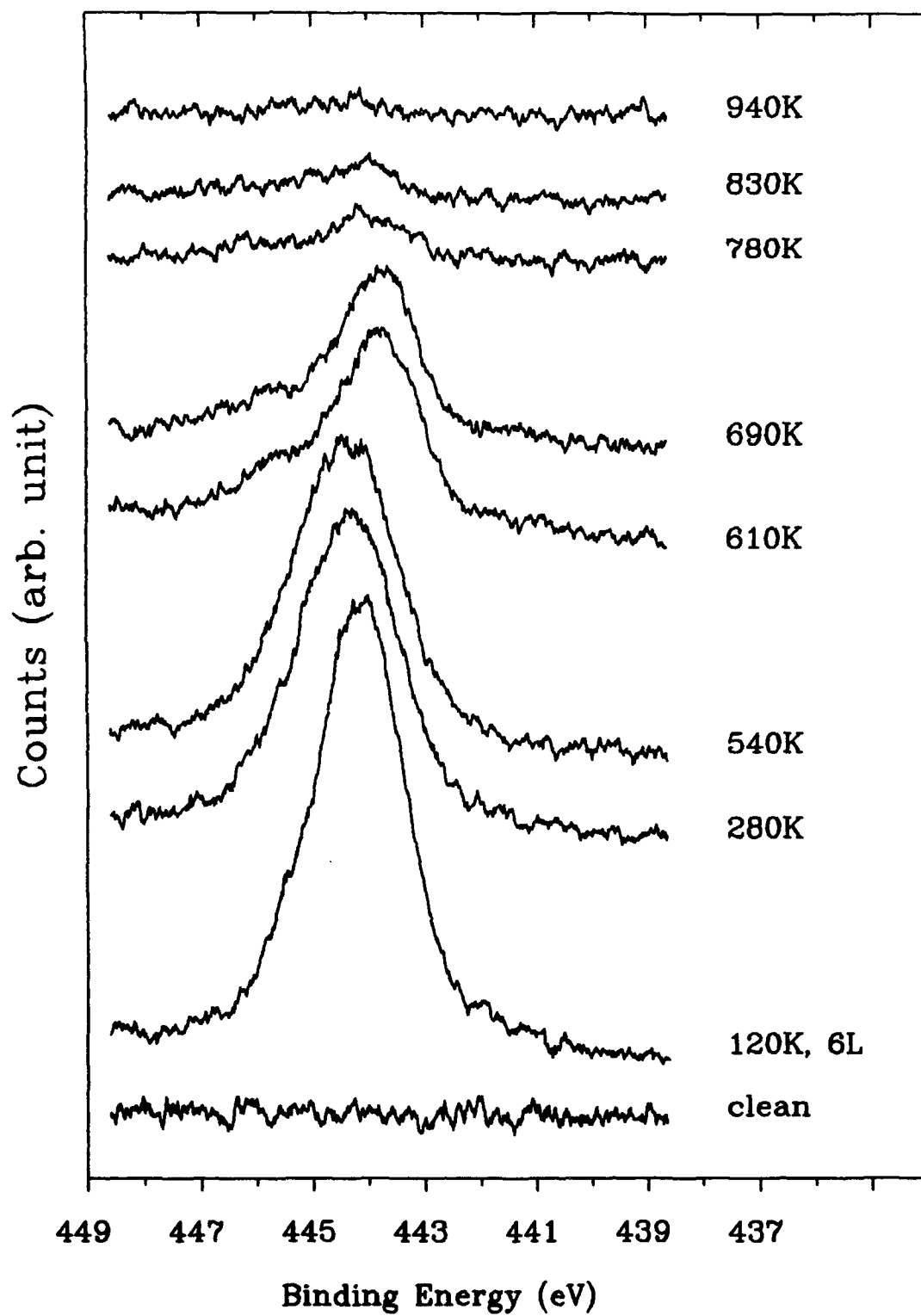


Fig. 1b

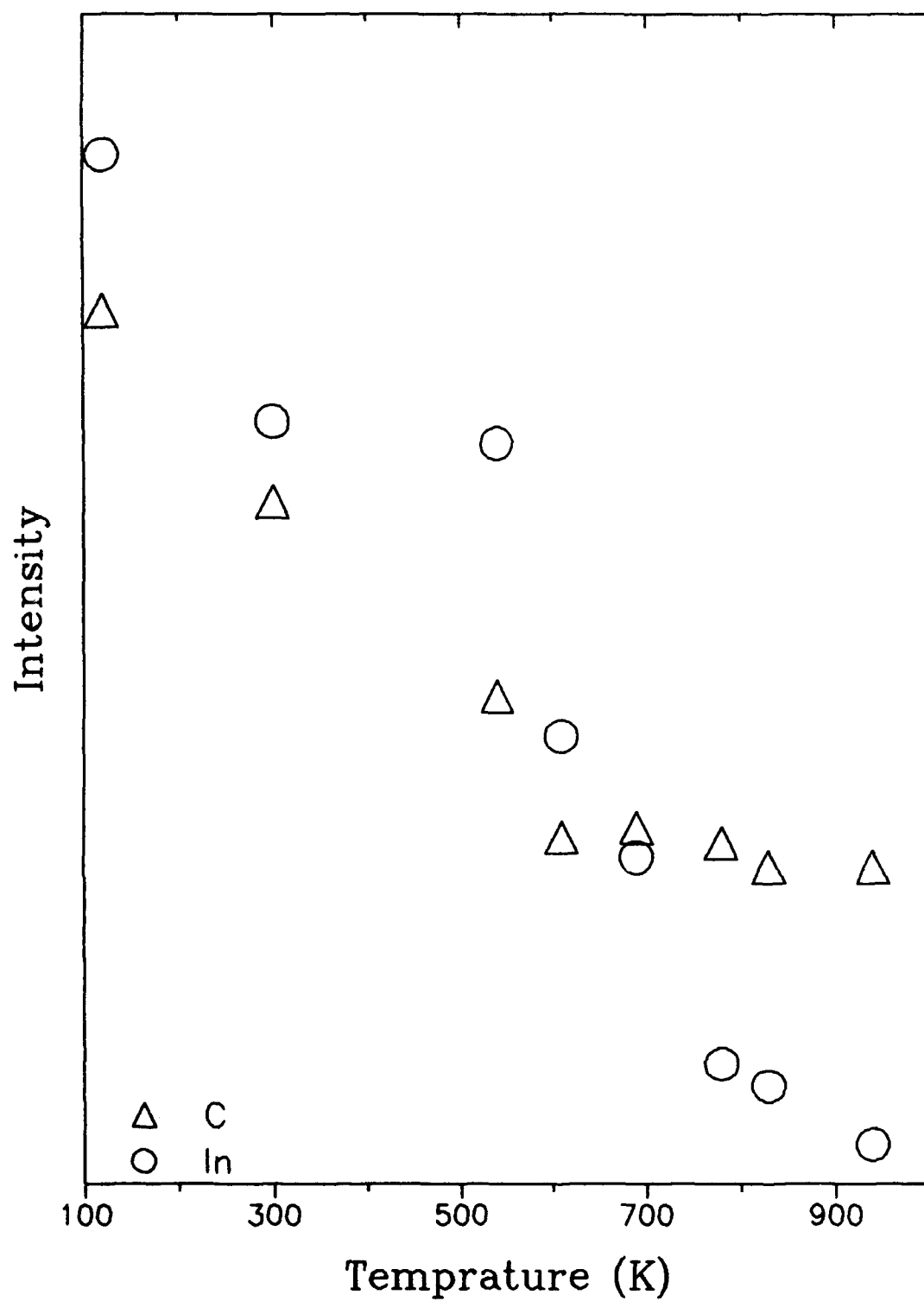


Fig. 2

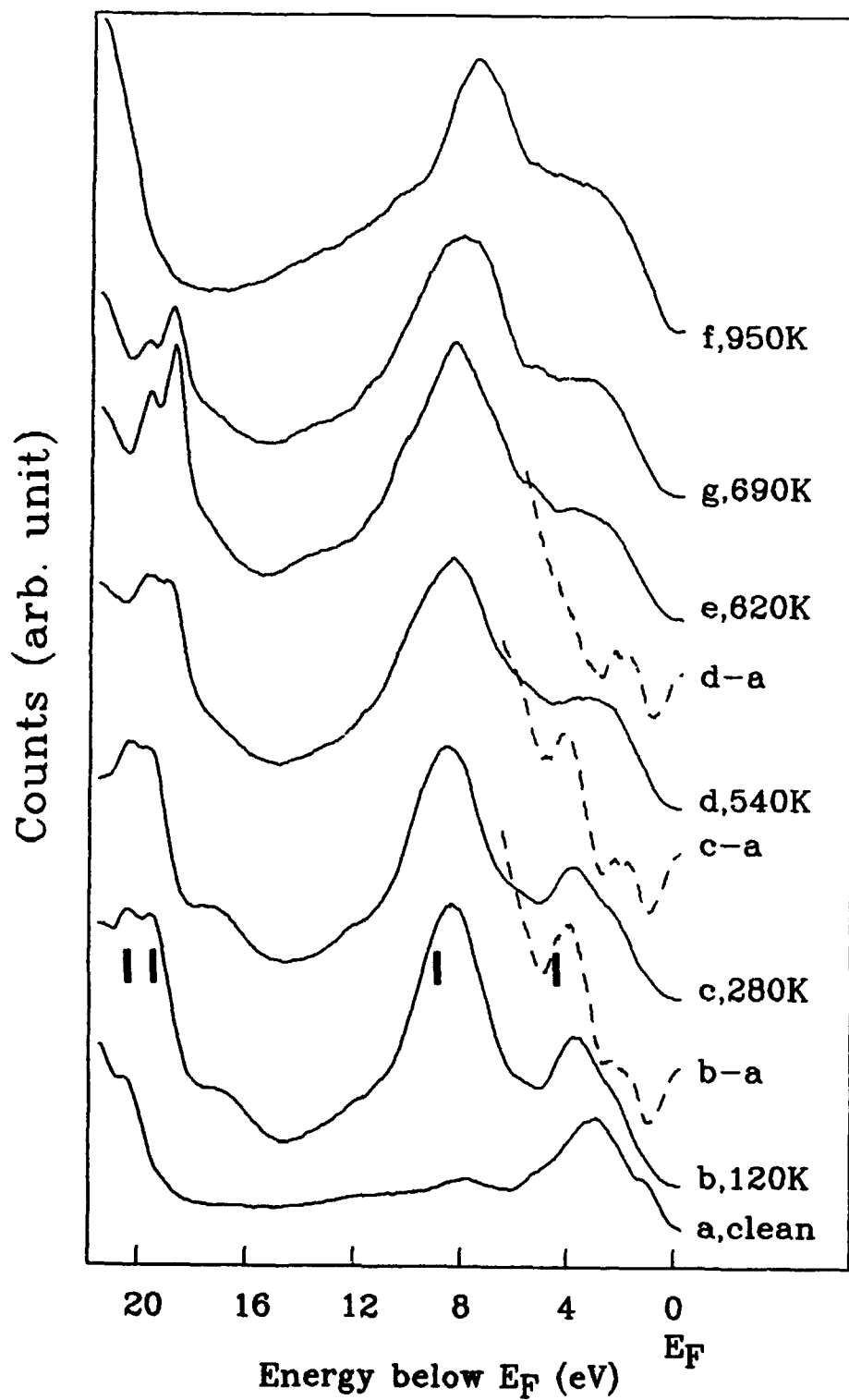


Fig. 3

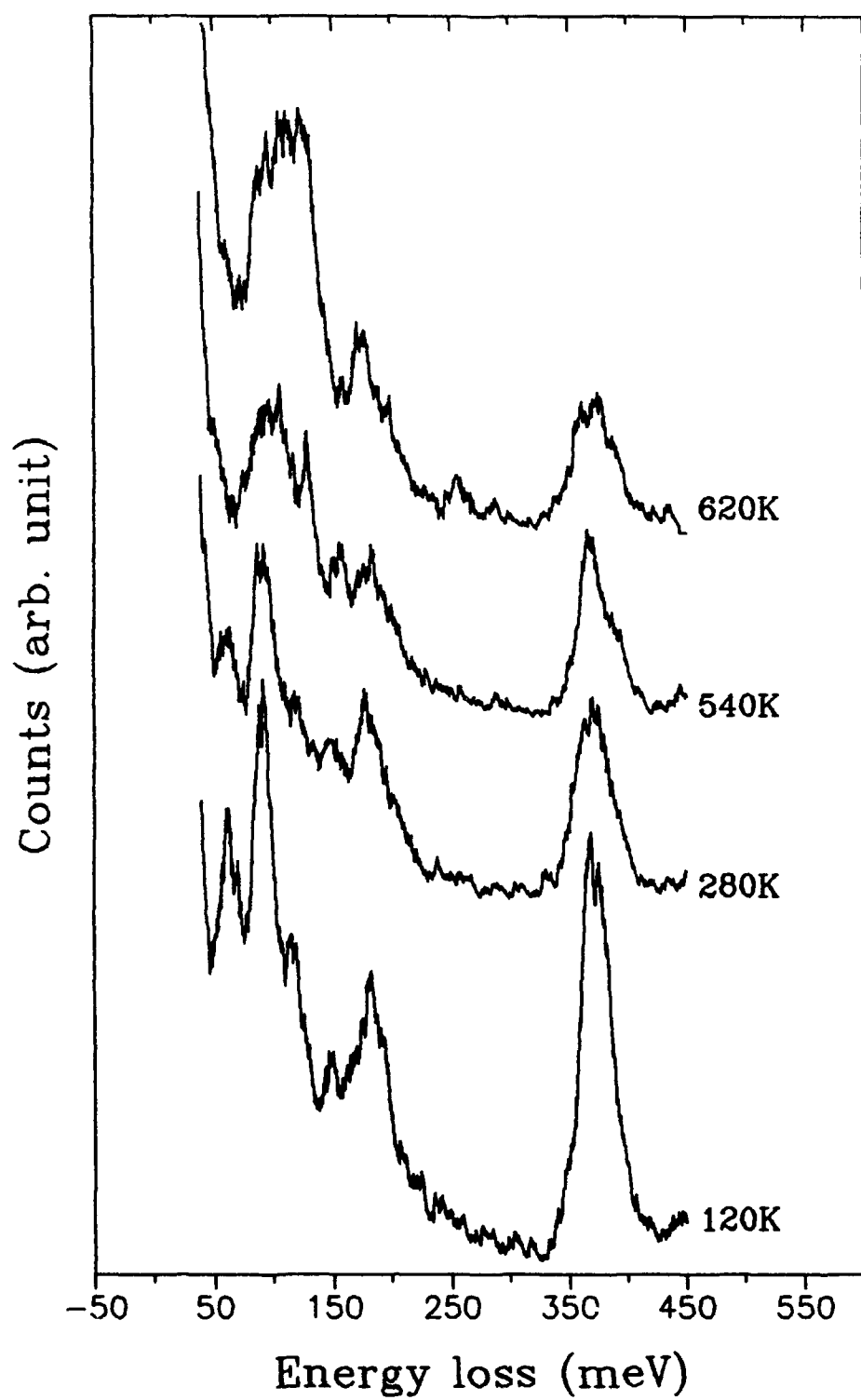


Fig. 4a

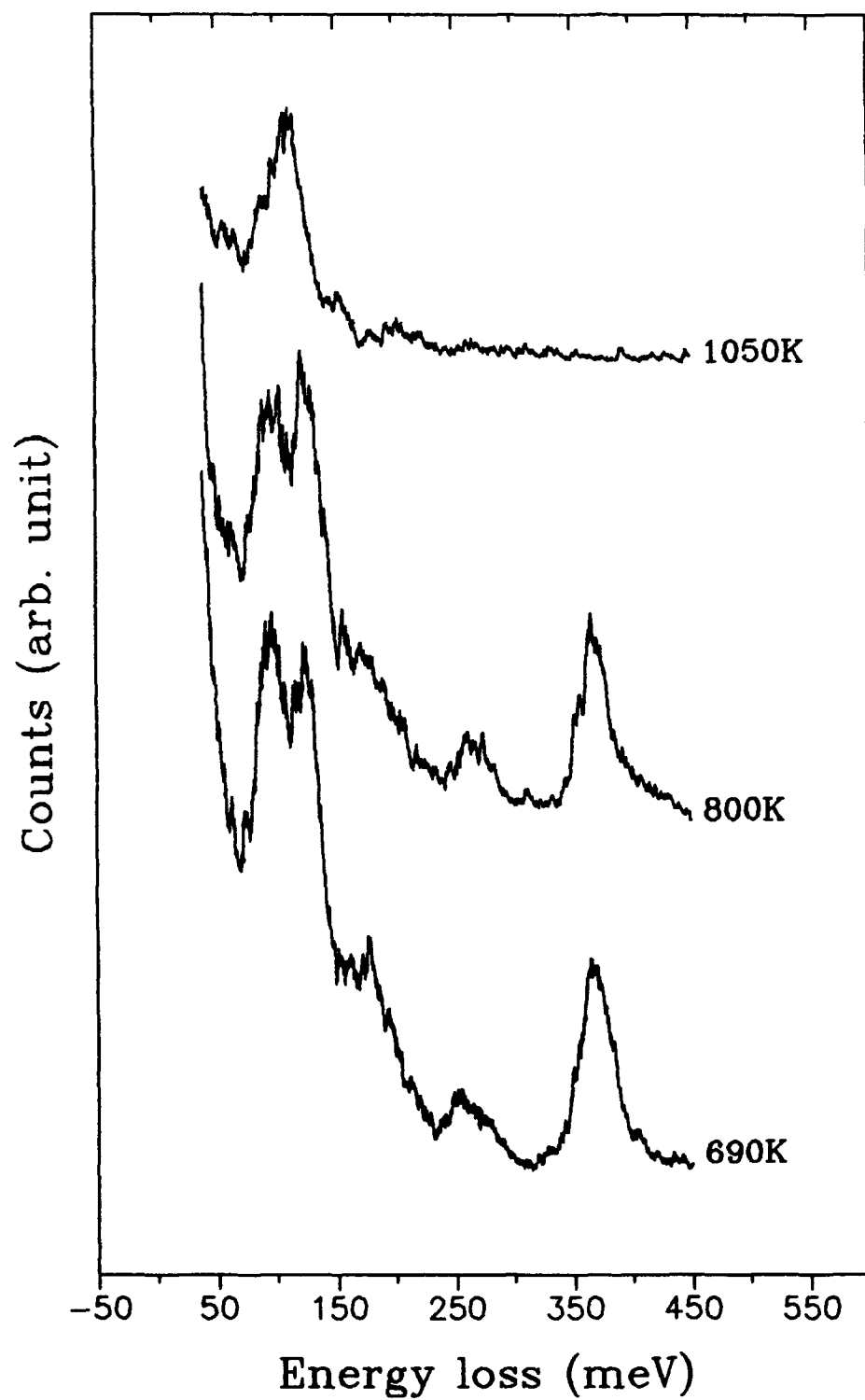


Fig. 4b