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Thermal Stability of Trimethyl Indium on Si (100)-2x1 As Studied with HREELS, UPS and XPS: A Comparison with the Results from Si(111)-7x7 and Si(110) Studies

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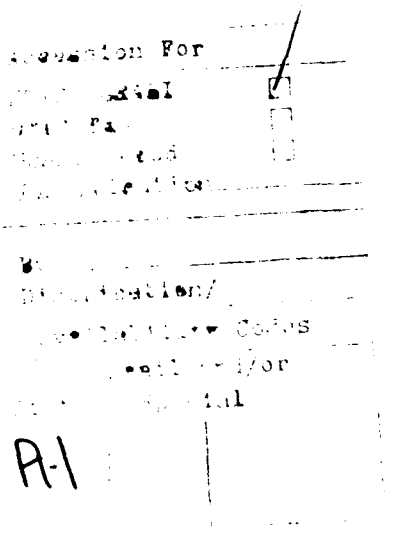

Abstract

The stability of trimethyl indium on the surface of a Si(100)-2x1 single crystal has been investigated with UPS, XPS and HREELS. The Si dangling bonds on Si(100)-2x1 was found to play an important role in the adsorption of TMIn, probably through the interaction with In 5 p_z orbitals and thus causing a distortion and possibly slight dissociation of the In-C bonds. However, the In-C bond breaking occurred to a much smaller extent on the (100) surface, if there is any, than on Si(110) and Si(111)-7x7. In the case of the (111) surface, TMIn attacks the adatoms before the rest-atoms. When 1L-dosed samples were annealed at 520 K, the In-C stretching vibration mode at 62 meV could still be observed in HREELS for TMIn on Si(100)-2x1, but not on the other two surfaces. Above 520 K, the In-C bond cracking was completed. Meanwhile C-H bond breaking also began to occur on the surface, which continued as the sample was further annealed at higher temperatures. At 950 K, only C species left on the surface following the decomposition of TMIn and the desorption of the In and H species.

Introduction

This study is part of our recent investigation to elucidate the mechanisms of group III-V semiconductor OMCVD (organometallic chemical vapor deposition) processes. This is an area of fundamental and technolcgical importance; its applications include optoelectronic and microwave devices, among others.[1] Earlier, we have reported the thermal decomposition of TMIn on Si(111)-7x7[2] and Si(110)[3]; HN_3 on Si(100)-2x1[4] and Si(110)[5] and N_2H_4 on Si (111)-7x7[6].

On Si(111)-7x7 and (110) TMIn was found to adsorb molecularly at 120 K with a partial breaking of the CH_3 groups from the In atom and an apparent distortion from its original planar geometry in the gas phase. The In-C bond cracking continued at 250 K and completed at temperature above 500 K. Further annealing of the samples caused the dissociation of the C-H bonds and the desorption of the In and H species.[2,3] In the present article, we report the results of TMIn interaction with Si(100)-2x1 at different temperatures; these results are compared with those of TMIn with Si(111)-7x7 and Si(110).

Experimental

The experiments were carried out in a custom-designed UHV system with multiple surface analysis capability as described elsewhere[2,6] . Si(100) single crystal from Virginia Semiconductor Corp. were cut into 1.5 x 1.0 cm^2 samples. As reported earlier, Si(100) surfaces are more difficult to clean than Si(111) [7,8]; a peak at ~100 meV due to C contamination could be readily observed in HREELS, even though XPS or AES showed it to be essentially clean. In the present work, the Si(100) sample was carefully cleaned by repeatedly flashing the sample at T > 1500 K until the peak at ~100 meV in HREELS disappeared entirely to avoid possible C-contamination effects. It should be pointed out that the elastic peak as well as the EEL signal

intensities are usually a few times stronger from Si(100)-2x1 than Si(111)-7x7, though the same straight-through electron beams were used.

TMIn (electronic grade) from Morton Thiokol Inc. was further purified by trap-to-trap distillation from room temperature to dry ice temperature. TMIn vapor from clear crystals was used in the experiment. The approximate dosage was estimated on the basis of the ion gauge reading without calibration for different gases.

3. Results and Discussion

3.1. The interaction between TMIn and Si at low temperatures

Figure 1 shows the HREELS of 1L TMIn on Si(100)-2x1 at 110 K taken in (a) specular and (b) 12° off-specular modes, respectively. As is evident in Figure 1a, peaks at 62, 86, 155 (shoulder), 179 and 365 were observed. By analogy to known IR/Raman TMIn spectra, these peaks can be assigned to the In-C stretching (υ_{In-C}), CH_3 rocking (ρ_{CH3}), CH_3 symmetric deformation (δ_{CH3}), CH_3 asymmetric deformation (δ_{a-CH3}) and C-H stretching vibrations, respectively, as summarized in Table 1. The corresponding IR/Raman data of TMIn measured in the gaseous and liquid phases are also included in the table for comparison.

The intense peak at 62 meV due to the υ_{In-C} vibrational mode is in good agreement with those obtained from IR/Raman spectra of TMIn. This suggests that TMIn molecularly adsorbs on Si(100) at 110 K. However, the strong peak at 86 meV (which deviates somewhat from its gas phase value) and, especially, the relatively strong δ_{a-CH3} peak at 179 meV (which is inactive in the IR/Raman spectra of TMIn) suggest that TMIn may be distorted from its planar structure upon adsorption and/or a possible slight dissociation of the In-C bonds as well. However, such an In-C bonds dissociation occurred to a much smaller extent, if any at all, as compared to the cases of TMIn adsorbed on Si(111)-7x7 and Si(110). This will be further discussed shortly.

Furthermore, the near absence of the 62 meV in the off-specular spectrum indicates that the υ_{In-C} mode is due mainly to dipole scattering; this could be caused by either the adsorbed nonplanar TMIn or the dissociated TMIn species [9]. Similarly, the δ_{a-CH3} mode, which becomes active upon adsorption, could also be caused by either the dissociation or the distortion of TMIn molecules or both.

Figure 2 summarizes the TMIn dosage effect on the surface states of Si(100)-2x1 by UPS. Obviously, the surface states were involved in the interaction between TMIn and the surface upon adsorption, as the peak at 0.8 eV below E_F was continuously attenuated with the increasing dosage of TMIn and essentially vanished at 1.0 L. According to the asymmetric dimer model for Si(100)-2x1, the surface states are originated from the "up atoms" dangling bonds, which are essentially filled with electrons and give rise to the peak at 0.8 eV below E_F in UPS[10]. The decrease in the intensity of the 0.8 eV peak implies that TMIn molecules actually adsorb on the "up atoms", at the top most layer of the Si(100)-2x1 surface. This is understandable, if one recalls that in the TMIn molecule the three valence electrons of the In atom ($5s^2$, $5p^1$) form bonds with three CH_3 groups and the remaining $5p_z$ orbital is essentially empty. In principle this empty orbital could form an additional bond with the dangling bond of an "up atom" by sharing the electrons from the latter. Such an additional bond would certainly cause the deformation of the TMIn molecule, i.e., pushing the three CH_3 groups upward, or even the dissociation of the In-C bonds. This type of adsorption geometry could explain the observed dipole scattering of the In-C stretching vibration and the fairly strong CH_3 asymmetric deformation vibrational mode as well.

Similar experiments were also carried out for TMIn on Si(111)-7x7 as shown in Figure 3. In this case, the situation is a little different, because there are two types of surface states, namely S_1 and S_2, originated from the dangling bonds on the "adatoms" and "rest-atoms", respectively. In an STM study, Avouris et al.[11] concluded that the rest-atoms are electron richer than the adatoms because of the

change transfer from the latter to the former. They also found that the rest-atoms are more reactive towards the adsorbed NH_3 at room temperature, which is also observed by Kubler et al.[12] in their UPS study of NH_3 on Si(111). In the present study, however, we found that the S_1 state was attenuated first and then the S_2 state as the TMIn was continuously introduced onto the Si (111)-7x7 surface at 110 K. This is clearly shown in Figure 3, where the peak at ~0.2 eV below E_F due to the S_1 state is essentially vanished at 0.3 L dosage; at this dosage the peak at 0.8 eV below E_F juststarted to decrease, but it vanished totally at ~1L.

When Si(111)-7x7 was exposed to atomic In, it was found that the In atom replaced the Si adatoms and formed bonds with the three Si atoms underneath leaving the In $5p_z$ orbital left essentially empty[13]. This is different from the case of TMIn on Si(111)-7x7, because In atom is still bonded to the CH_3 groups upon adsorption as discussed above on HREELS results. In addition, the S_3 state, originated from the backbond between the adatoms and the Si atoms underneath them, was hardly affected when the surface was exposed to 1L of TMIn while both S_1 and S_2 states were substantially attenuated. The interaction between TMIn and the Si(111) surface should be similar to the case of TMIn on Si(100)-2x1, involving the $5p_z$ orbitals of the In atoms and the dangling bonds on adatoms and rest-atoms. Unfortunately, such an In-Si vibrational mode could not be observed in the HREELS with the resolution used here because of the large tail of the elastic peak. Similarly, Ga-Si and Al-Si vibrational modes were also not observed in HREEL spectra of TMGa[7] and TMAl[14] on Si substrates. It should be pointed out that the interaction between the In atom and the Si surface may also involve the In 4d electrons as discussed earlier in reference [3].

Figure 4 compares the HREELS of TMIn on Si(100)-2x1, Si(111)-7x7 and Si(110) upon adsorption at 110 K. The relative intensity of the In-C stretching vibration peak at ~62 meV is the strongest on Si(100) and the weakest on Si(110).

This is probably due to the fact that TMIn adsorbs on the three surfaces with different degrees of dissociation and that its orientations on these surfaces are different. Niwano et al. [15] found that oxygen react differently with Si(111), Si(110) and Si(100) because of the different bond topology on the three surfaces, i.e., surface Si atoms have one unsaturated broken bond on Si(111) and Si(110) and two broken bonds on Si(100). The Si(110) surface produced more Si^{3+} oxidation states as compared with Si(111) and Si(100), because the number of Si-Si bonds on the outermost layer of Si(110) is relatively large and these surface Si-Si bonds are readily broken by the atomic oxygen upon adsorption. These observations are essentially consistent with our results: at 110 K TMIn dissociated readily on Si(110), to some extent on Si(111) and only slightly on Si(100).

Si(111) was also found to be more reactive than Si(100) for the further decomposition of the NH_2 produced from NH_3 dissociative adsorption, because the back bonds associated with the adatoms on Si(111) are easier to break than those associated with the dimer atoms on Si(100)[16]. Here we found that Si(110) is the most effective surface for the dissociative adsorption of TMIn. This is probably because that there are more adatoms on Si(110), (e.g. a 4 x 5 reconstructed surface) [17] , than on Si(111)-7x7. In addition, the surface defects may also play important roles on the dissociative adsorption of TMIn. In the present studies, all surfaces were cleaned by high temperature annealing (≥1500 K), this process usually creates defects on Si surfaces. Unfortunately, such surface defects could not be detected by our present experimental setup.

The adsorption geometry of TMIn on the surface could also affect the relative intensity of the $\upsilon_{In\text{-}C}$ peak. Since TMIn interacts with the Si dangling bond, the orientation of the latter would certainly affect the TMIn adsorption geometry. For Si(111)-7x7, the dangling bonds from both the "adatoms" and the "rest-atoms" are perpendicular to the surface plane according to the "dimer-adatom-stacking fault"

model [18]. For Si(110), which showed a complicated LEED pattern with 4 x 5 spots stronger than the rest in our experiments, most of the dangling bonds are also perpendicular or nearly perpendicular to the surface plane. For Si(100)-2x1, on the other hand, the dangling bonds from the Si dimer atoms are tilted from the surface normal. If there were no distortion or dissociation upon adsorption, the TMIn molecular plane would be parallel to Si(111)-7x7 or Si(110) and slightly tilted on Si(00)-2x1. Thus a relatively strong $\upsilon_{In\text{-}C}$ peak would be expected for TMIn on Si(100)-2x1 as compared to Si(111)-7x7 or Si(110). Such a tilted adsorption was indeed found for chlorine on Si(100)-2x1 [19]. It should be pointed out that the adsorption geometry may also affect the relative intensity of the other vibration peaks, such as the CH_3 symmetric and asymmetric deformation, as discussed earlier by Narmann et al. for TMGa on GaAs surfaces .

3.2. Thermal decomposition of TMIn on Si(100)

When the 1L TMIn dosed Si(100) was warmed to 250 K, no significant changes in HREELS was observed, except the attenuation of all the peaks (see Figure 5). This is probably a reflection of the partial desorption of TMIn, which is more obviously indicated by the corresponding XPS results. Both $In_{3d\ 5/2}$ and C_{1s} peak intensities were attenuated and the results are essentially identical to those of TMIn on Si(111) and Si(110) discussed earlier [2,3]. On the other hand, the similarity between the HREELS at 110K and 250K indicates that there is no further In-C bond cracking at 250K. This, in turn, suggests that there is no significant In-C bond at 250K However, we cannot rule out the possibility of the In-C breaking, which may occur at surface defects upon the adsorption. As the surface was annealed at 520 K, the following changes were noticed, indicating the dissociation of the In-C bonds. Firstly, the In-C stretching vibration peak at 62 meV almost vanished. In addition, shoulders at 105

and 118 meV could be identified. The former could be attributed to the rocking vibration of the CH_3 groups attached to the surface as discussed in detail for TMIn on Si(111)[2], where the 105 meV peak was much more intense. The vibration mode at 118 meV might be due to the twisting vibration of the CH_2 groups, which was also observed by Lee et al. [7] for TMGa on Si(100).

Secondly, the relative intensities of the 86 and 155 meV peaks were enhanced and the 86 meV peak also shifted to 90 meV. The changes of the 86 meV peak is due to the splitting-off of the CH_3 groups from the In atom to the substrate and thus there is more contributions from Si-C stretching vibration to the peak. The dissociation of the In-C bonds could also enhance the 155 meV peak intensity because of the CH_3 orientation change. It may be partially due to the presence of the CH_2 species, which was found to show peaks at 112, 156, and 179 meV corresponding to the rocking, wagging and scissoring vibrations, respectively, as reported in a study of C_2H_4 on Si(100)[20].

Further annealing the sample at 680 K caused the complete dissociation of the In-C bonds as indicated by the disappearance of the In-C stretching mode at 62 meV. Meanwhile, the shoulder at 118 meV shifted to 124 meV and became a distinct peak, and the relative intensities of the 90 and 155 meV were further enhanced. In addition, a new peak at 260 meV due to the Si-H stretching vibration appeared. These changes could be related to the further cracking of the C-H bond and thus forming CH_X ($X \leq 3$) and H species on the surface. The presence of H on the surface is clearly evidenced by the Si-H stretching mode at 260 meV, while the increase in the relative intensity of the 124 and 155 meV peaks may suggest the formation of the CH species on the surface, because peaks at 120 and 156 meV for CH bending modes (ρ_a and δ_α) were observed for C_2H_2 on Si(100) by Nishijima et al.[21] Further cracking of the C-H bonds at 800 K was indicated by the intensity increase of the Si-H stretching mode at

260 meV. At 950 K, the HREELS was dominated by a peak at ~100 meV due to the Si-C stretching vibration.

The thermal decomposition process of TMIn on Si(100)-2x1 is essentially the same as those observed for TMIn on Si(111)-7x7 and Si(110), except that the In-C bonds cracking occurred to a lesser extent for TMIn on Si(100) than on Si(110) or Si(111) at the same temperatures. Additionally, at 520 K, the 105 meV peak in HREELS is much more intense on Si(111) than on the other two surfaces, probably indicates that the CH_3 groups are more stable on Si (111). The different reactivity of small molecules, e.g. NH_3, on Si (111)-7x7 and Si(100)-2x1 has been recently studied fairly extensively[11,16]. However, such a subtle difference was hardly reflected by the corresponding UPS and XPS results; accordingly, these data on the decomposition of TMIn on Si(100)-2x1 are not presented here.

Conclusion

The adsorption and the thermal decomposition of TMIn on Si(100)-2x1 were studied with HREELS, UPS and XPS. TMIn was found to adsorb on Si(100) at 110 K through interaction between the dangling bond on the "up-Si-atom" and the In $5p_z$ orbital. The interaction caused the distortion of the TMIn from its original planar structure and probably some breaking of the CH_3 groups from the In atom onto the surface. However, the dissociation of the In-C bond occurred to a much lesser extent, if any at all, as compared with the cases of TMIn on Si(111)-7x7 and Si(110). This is further illustrated by the thermal annealing process. At 250K, there were no obvious changes in HREELS except the attenuation of all peaks and at 520 K, the In-C stretching mode was still visible for TMIn on Si(100), but not on the other two surfaces. Above 520 K, the In-C bond breaking was essentially complete and the cracking of the

C-H bonds also took place on the surface. At T≥950 K, only C left on the surface following the decomposition of TMIn and desorption of the In and H species.

Acknowledgements

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Table 1. The vibrational frequencies of TMIn in the gas/liq phases (IR/Raman) and adsorbed on Si substrates.

Mode	In $(CH_3)_3$ [a] IR	In $(CH_3)_3$ [a] Raman	In $(CH_3)_3$ [b] on Si(111)-7x7	In $(CH_3)_3$ [c] on Si(110)	In $(CH_3)_3$ [d] on Si(100)-2x1
C-H str.	372 362	369 361	368	368	365
CH_3 asym. def.			181	180	179
CH_3 sym. def.	143	143 138	154	153	155
CH_3 rock.	90 85	90 80	88	92	86
In-C str.	62	62 58	63	61	62
In-C def.		16			

a. J. R. Hall, L. A. Woodward and E. A. V. Ebsworth; Spectrochim Acta, 20 (1964) 1249; A. J. Blake and S. Cradock, J. Chem. Soc., Dalton Trans. 2393 (1990).
b. ref. 2
c. ref. 3
d. this work

Figure Captions

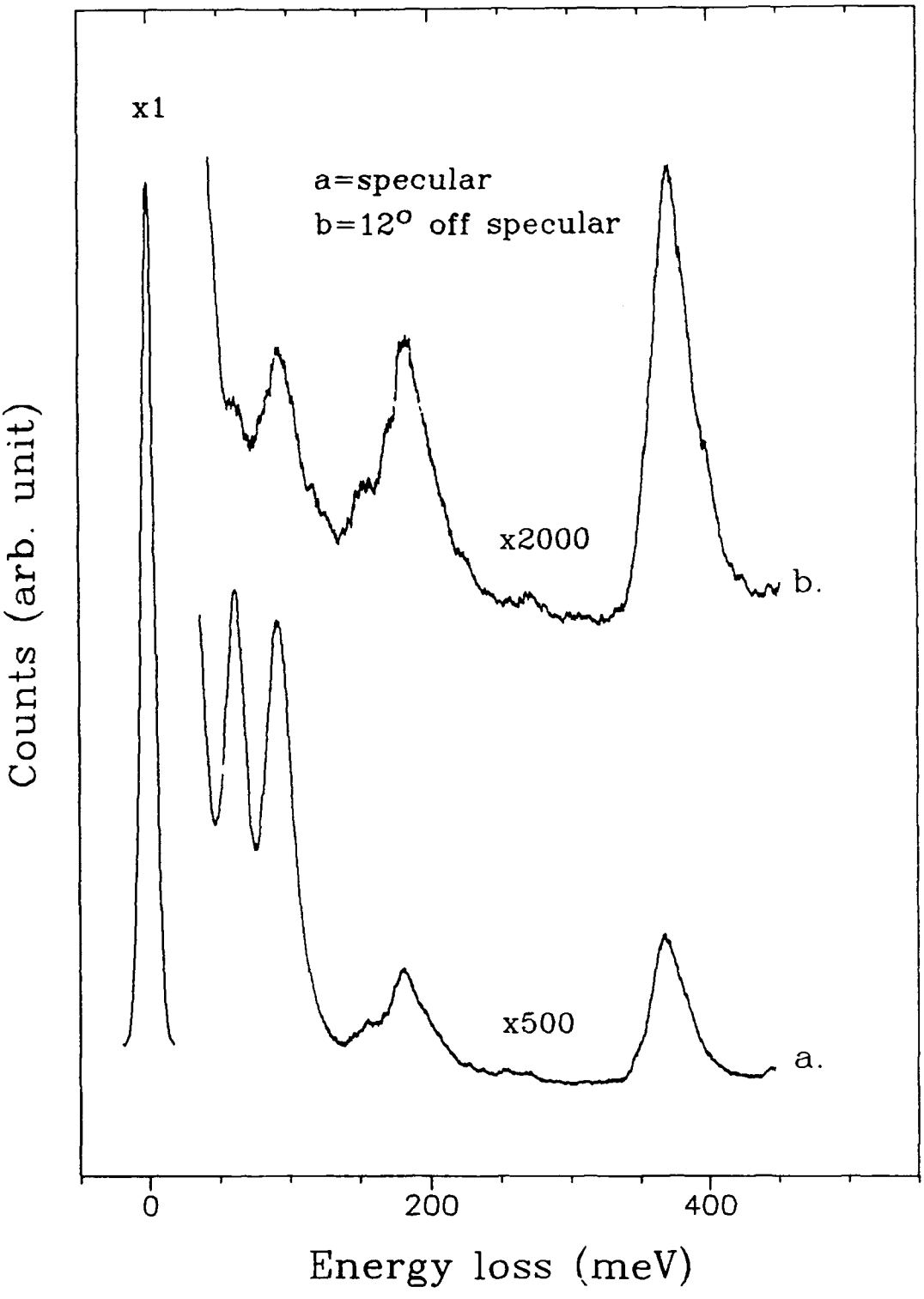
Figure 1. HREELS of 1L TMIn dosed Si(100)-2x1 at 110 K taken in the (a) specular, and (b) 12° off specular modes.

Figure 2. A series of He(I) UPS spectra taken at 110 K showing the TMIn dosage effect on the Si(100)-2x1 surface states.

Figure 3. A series of He(I) UPS spectra taken at 110 K showing the TMIn dosage effect on the Si(111)-7x7 surface states.

Figure 4. HREELS of TMIn adsorbed on Si(100), (111) and (110) surfaces at 110K.

Figure 5. HREELS of 1L TMIn dosed Si(100)-2x1 recorded at 110 K after annealing the sample at the indicated temperatures.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b.
x500
a.
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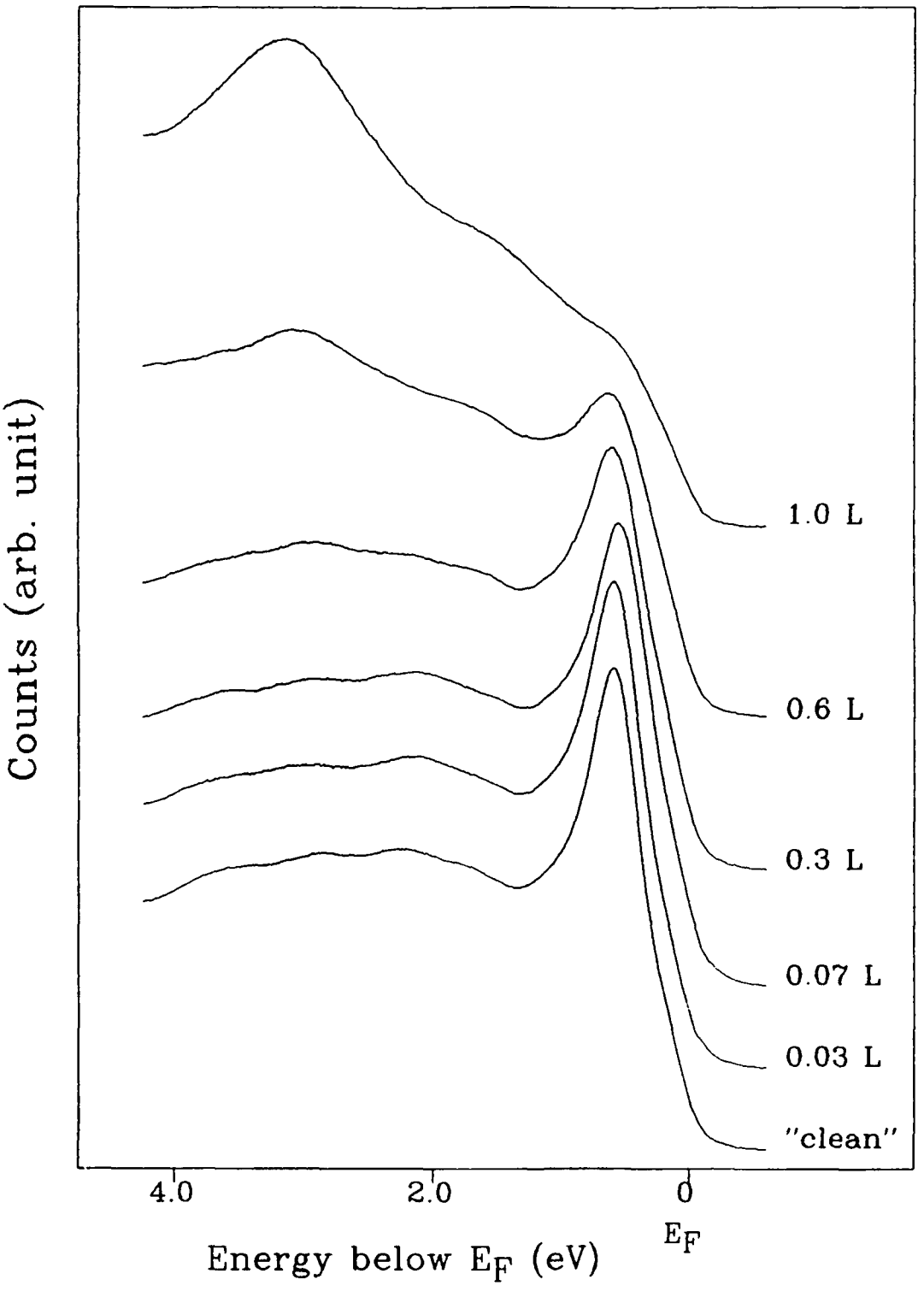
200
400
Energy loss (meV)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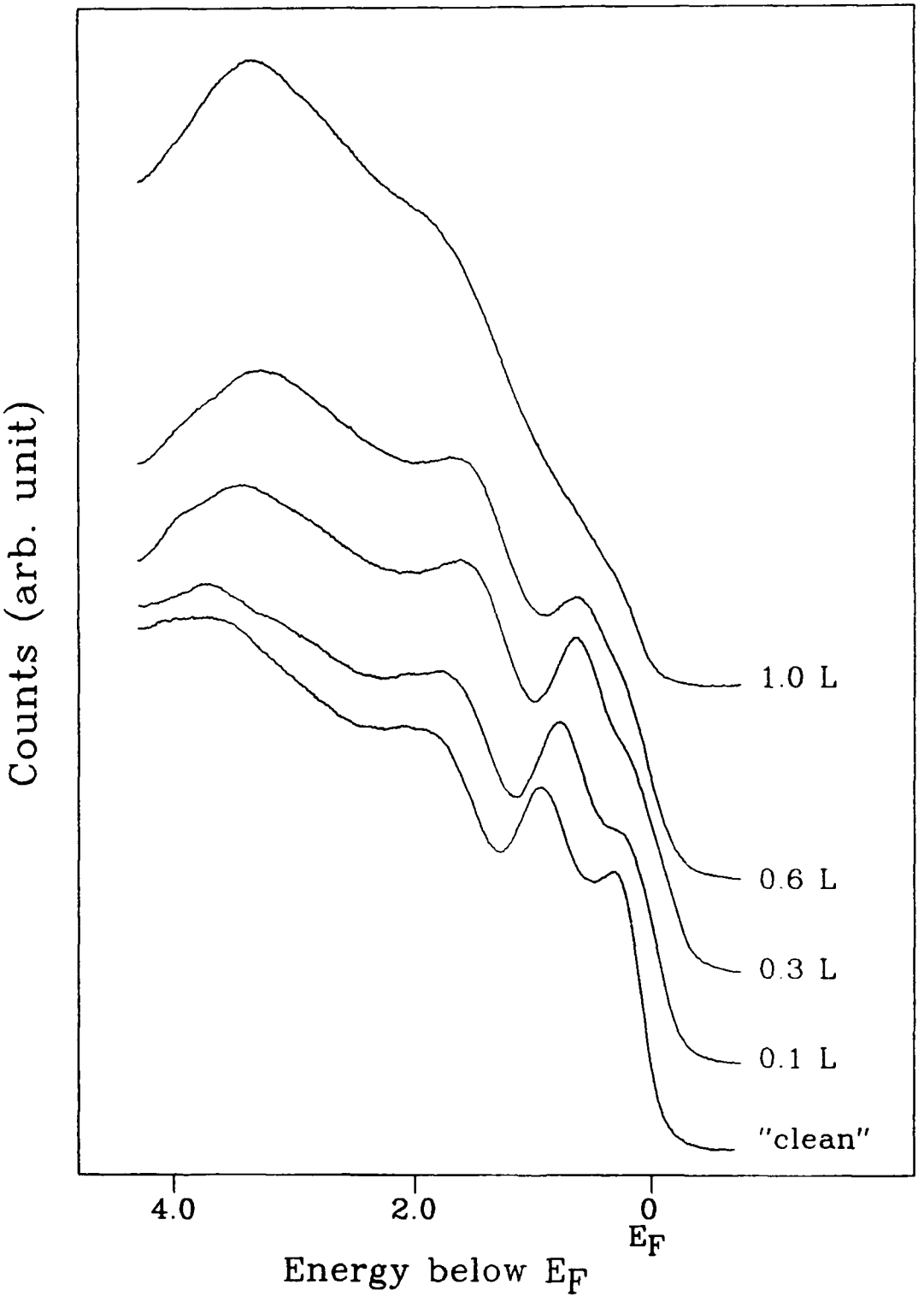
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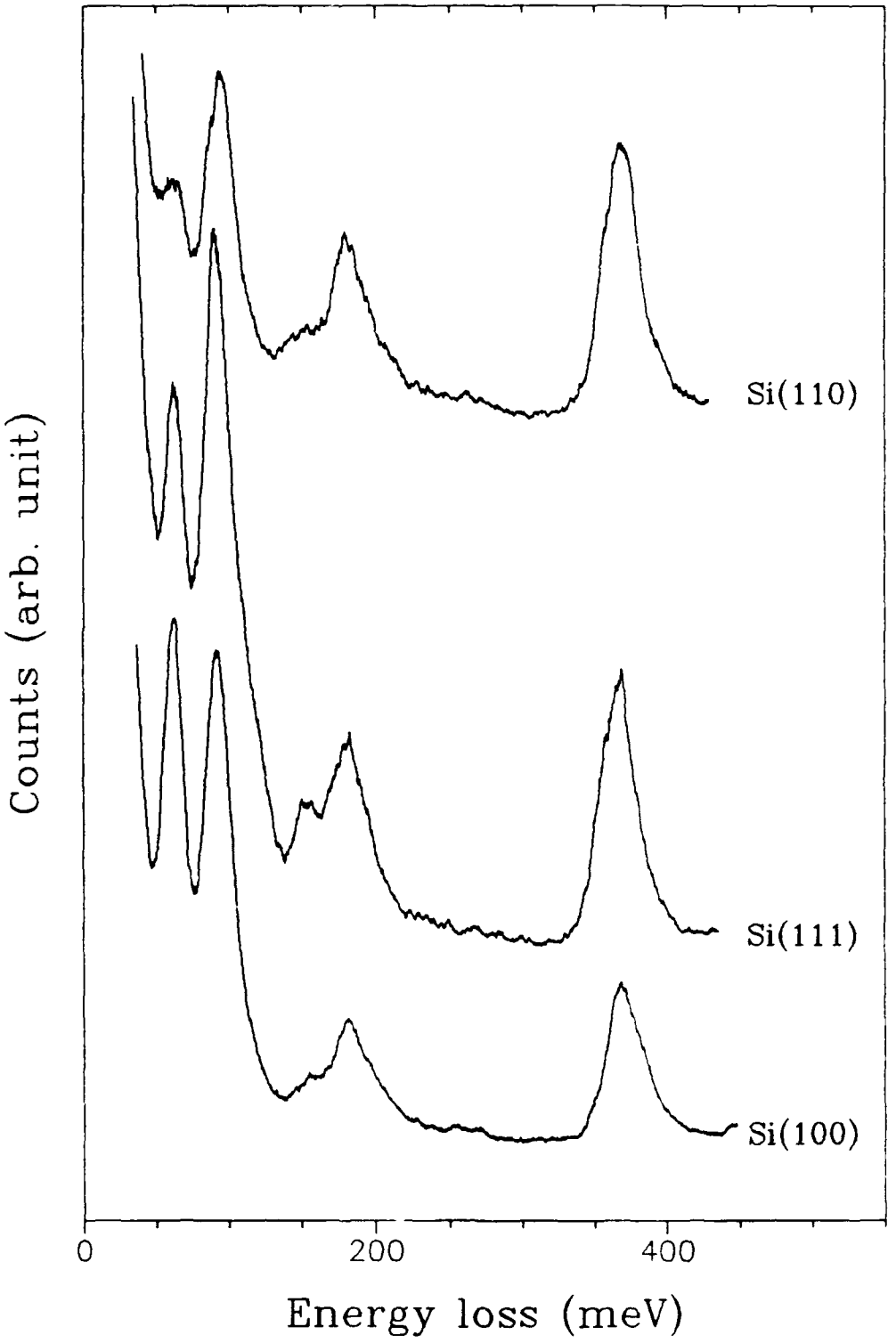
0
E_F
Energy below E_F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Si(100)
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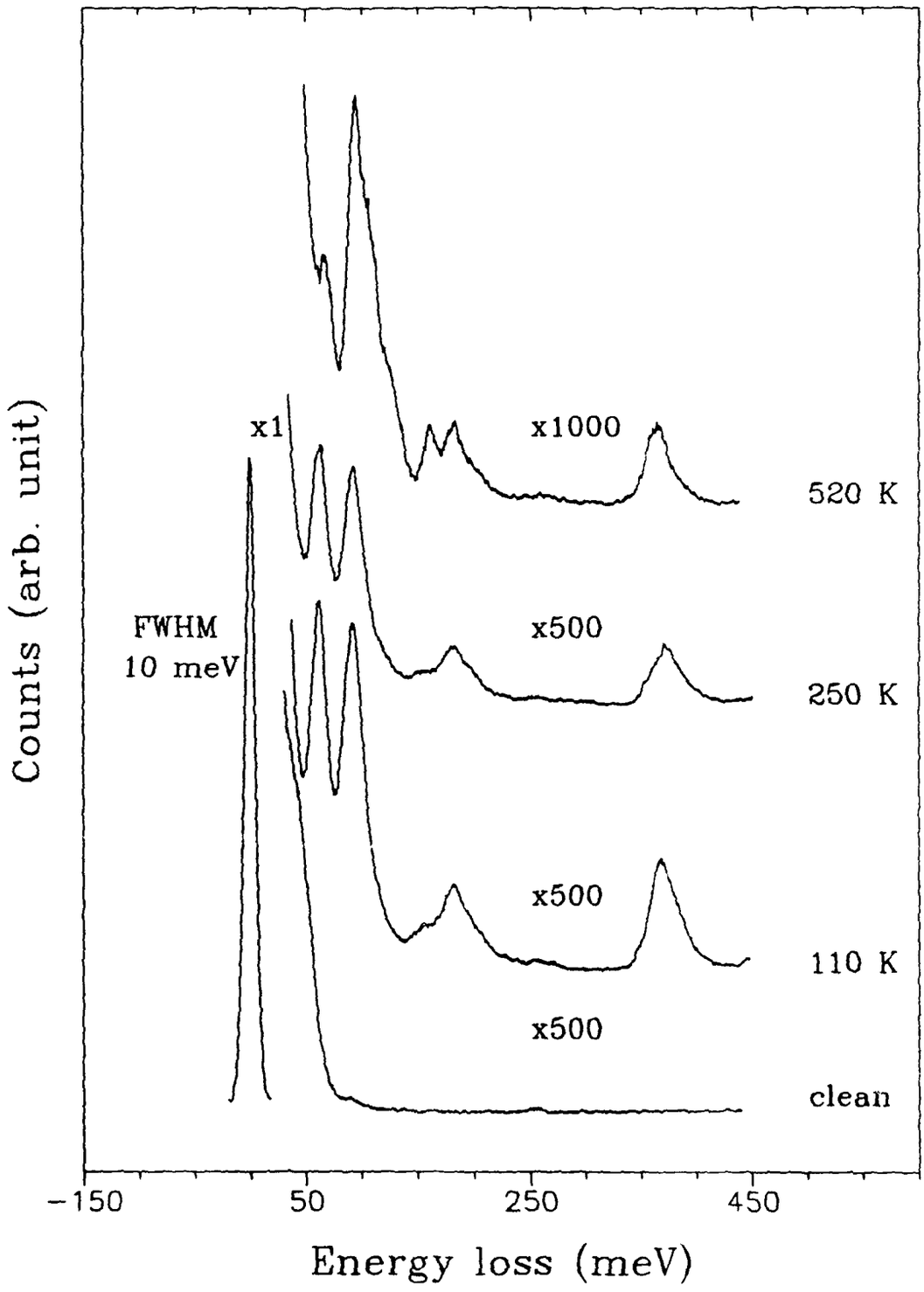
400
Energy loss (meV)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x500
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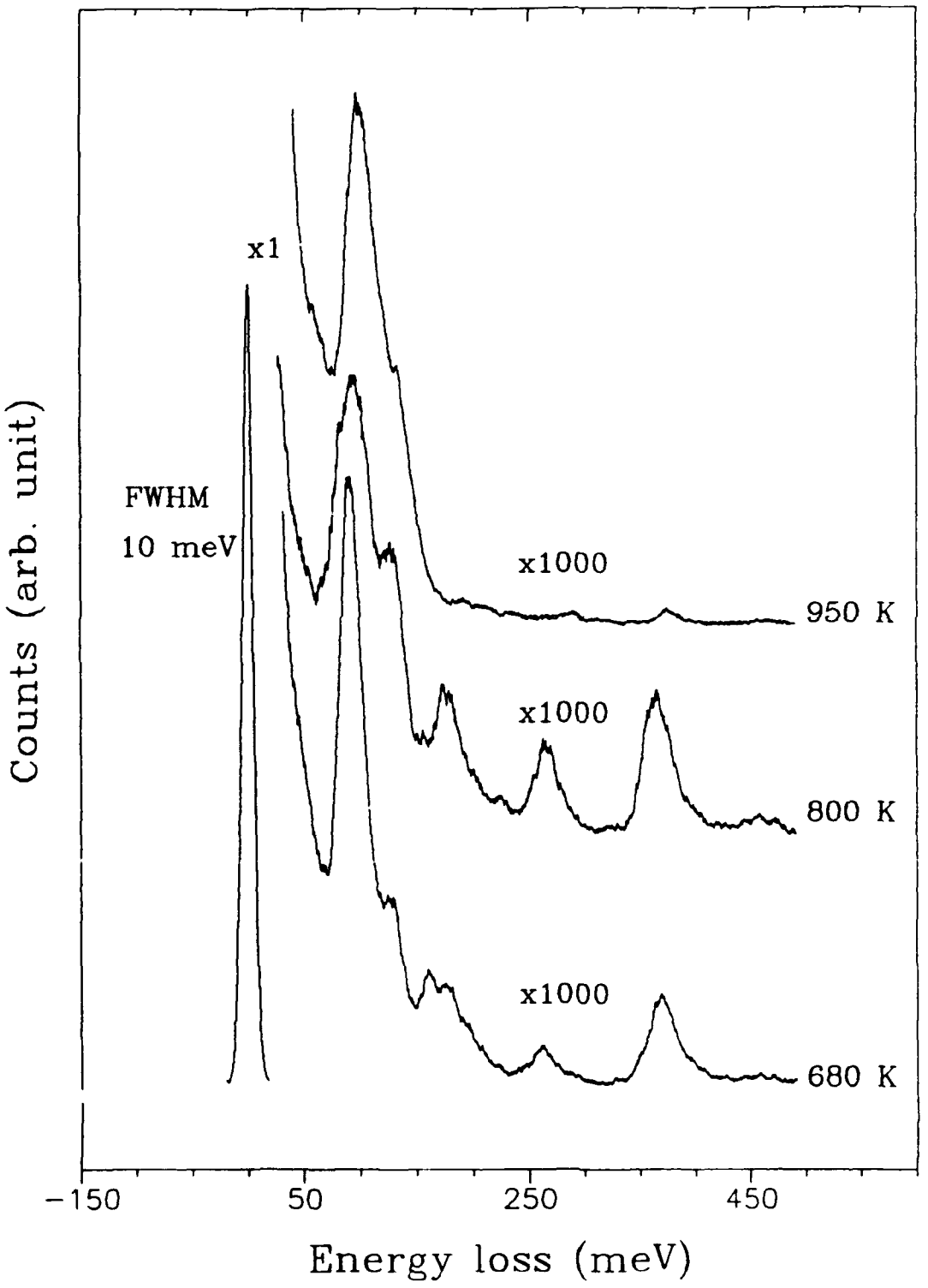
x500
110 K
x500
clean
−150
50
250
450
Energy loss (meV)


x1
FWHM
10 meV
x1000
950 K
x1000
800 K
x1000
680 K
Counts (arb. unit)
−150
50
250
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Energy loss (meV)