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Low-energy electron-loss spectroscopy of GaSe and InSe

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Low-energy electron-loss spectra (LEELS) of GaSe and InSe have been measured for what we believe to be the first time. Both crystals produced very similar spectra, indicating the similarity of the electronic structures of these compounds. Ten loss peaks were observed in the second derivative of the LEELS spectrum. Two of these are associated with collective excitations of the valence electrons, namely, the bulk and surface plasmons. The peaks related to the excitation of Ga $3d$ (In $4d$) core electrons have three final states in the conduction band. The other five peaks are explained by transitions from the Se $3d$ core level and the valence band, whose final states coincide with those for the Ga $3d$ (In $4d$) level. The spectrum from the Ar^+-ion-sputtered surface showed bulk and surface plasmon losses for a metal, i.e., Ga in GaSe and In in InSe, respectively. This result indicates that the surface of these crystals is changed to a metallic state by Ar^+-ion sputtering.

I. INTRODUCTION

The crystal structures of the III-VI layered semiconductors GaS, GaSe, and InSe are described by stackings of thin layers. A single layer consists of four atomic planes in the sequence X-M-M-X (X =S, Se, M =Ga, In).[1] The interlayer interactions are very weak compared to those inside a single layer.[2] The electrical and optical properties related to this anisotropic crystal structure have been extensively investigated for many years.[3]

The band structures have been calculated by Kamimura and Nakao (tight-binding method for π bands),[4] Bassani and Parravicini (two-dimensional tight-binding method),[5] Schlüter, and Schlüter and Cohen [three-dimensional empirical pseudopotential method (EPM)],[6,7] and Doni *et al.* [three-dimensional overlap-reduced semiempirical tight-binding method (ORSTB)],[8] and compared with the optical reflectivity data.[9–11]

Direct information on the density of states of the valence band have been obtained by ultraviolet photoelectron spectroscopy[12–15] (UPS) and x-ray photoelectron spectroscopy[13,16–18] (XPS). Using synchrotron radiation UPS, Margaritondo *et al.*[15] have observed four main peaks in the density of states of the valence band for GaS, GaSe, and InSe between the top of the valence band and the cation d core level. In addition to the valence-band structures, they have obtained the density of states of the conduction band above the vacuum level by observing constant initial state (CIS) spectra. The results were interpreted by the EPM band calculation for GaSe.[6] Antonangeli *et al.*[18] have measured XPS spectra of GaS, GaSe, and InSe, by using unmonochromatized Al $K\alpha$ x rays as the excitation source. They have observed five structures in the valence-band region, and compared the results with the density-of-states functions derived from the ORSTB band structures.[8] Angle-resolved photoemission spectroscopy using synchrotron radiation has also been applied to GaSe and InSe to study the dimensionality of the band structure.[19,20]

Electron energy-loss spectroscopy has also been used to investigate the electronic structure of these crystals.[21–23] Soukiassian *et al.*[22,23] have measured the energy-loss spectra of GaSe and InSe using a 40-keV electron beam, and, by means of a Kramers-Kronig analysis of the loss spectra, deduced the complex dielectric functions in the energy region from 3 to 35 eV. The results were discussed in relation to the EPM band structure.[6]

On the other hand, to our knowledge, a low-energy electron-loss spectroscopy (LEELS) study has not yet been done in these crystals. Since the sensitivity of LEELS is limited to the surface region (a depth of ~5 Å for a primary energy of ~100 eV), LEELS has recently been successfully applied to distinguish the intrinsic surface states[24] and the interface states in the early stage of metal-semiconductor[25] and semiconductor-semiconductor[26] interface formation.

In the present paper, LEELS measurements on GaSe and InSe are reported for the first time. The results should give useful information for further studies of interface formation between these crystals and metals or semiconductors, which is of great interest from the viewpoint of an ideal Schottky barrier,[27] and/or abrupt heterojunction[28] formation. Losses related to the intrinsic surface states are not observed, since no dangling bonds exist on the cleaved surface of these crystals. The origin of the observed losses will be discussed, by comparing the results with the bulk and surface loss functions calculated from the optical data,[11] and with the XPS spectra of the valence band and the core levels. In the previous paper,[29–31] we have shown that Ar^+-ion sputtering on the cleaved surface of GaSe and InSe changes the surface to a thin metallic layer, which is confirmed here by observation of bulk- and surface-plasmon losses on the sputtered surface.

II. EXPERIMENTAL PROCEDURE

GaSe and InSe were grown by the Bridgman method from the melt in a quartz ampoule of diameter 12 mm evacuated to 10^{-6} Torr. GaSe was *p* type with a carrier density of 1.5×10^{15} cm^{-3} and a mobility of 36 cm^2/V sec, while InSe was *n* type with a carrier density of 1.0×10^{14} cm^{-3} and a mobility of 450 cm^2/V sec, at room temperature. The crystal was cleaved and cut into a square of about 7×7 cm^2 in the basal plane. After the sample was mounted on the sample holder by silver paint, it was again cleaved with an adhesive tape just before insertion into the vacuum chamber.

Measurements were carried out using a conventional XPS—Auger electron spectroscopy system (ULVAC-PHI model 548SH) equipped with a double-pass cylindrical mirror analyzer (PHI model 15-255G) in a high vacuum chamber ($\sim10^{-9}$ Torr). LEELS spectra were measured in the AES mode of the system. The second derivative of the loss spectrum was obtained by modulating the deflection voltage and observing the second harmonic with a peak-to-peak modulation voltage of 2 eV, by using a lock-in amplifier (PHI model 9503). The primary electron beam energy was 40—200 eV, and the angle of incidence was 30° with respect to the sample surface normal. The surface contamination was checked by using the analyzer in the conventional AES mode. XPS spectra of the core levels and the valence band were measured by using unmonochromatized Mg $K\alpha$ x rays (1253.6 eV) as the excitation source. The binding energy was recorded with respect to the Fermi level referred to the Au $4f_{7/2}$ core level (83.5 eV). For the measurement of the valence band, the data were accumulated for about 20 h.

Ar$^+$-ion sputtering was performed at the condition of an emission current 25 mA, and a beam voltage of 0.5 kV for the study of sputtering effects on LEELS spectrum, and 5 kV for the removal of surface contaminations on In and Ga metals.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the second-derivative LEELS spectra of cleaved surfaces of GaSe and InSe up to an energy loss of 60 eV measured at a primary energy $E_p=100$ eV. Both crystals yield similar spectra consisting of ten loss peaks denoted *A*—*J*. This indicates the similarity of the electronic structures of GaSe and InSe. The peak energies of each loss are tabulated in Table I. The LEELS spectrum in these energy regions is considered to include losses due to the excitations of upper core levels, valence band, and collective modes (plasmons).

A. Plasmon excitations

Consider first plasmon excitations. Figure 2 compares the LEELS spectrum of GaSe at $E_p=100$ eV with the second derivatives of the bulk loss function $-\mathrm{Im}(1/\epsilon)$ and surface loss function $-\mathrm{Im}(1/\epsilon+1)$, in the energy range up to 30 eV. In the calculations of the second derivatives of bulk and surface loss functions, the real part ϵ_1 and imaginary part ϵ_2 of the dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ of GaSe are taken from the optical data in the literature.[11] A similar comparison for InSe is shown in Fig. 3. These figures show that the overall structures of $-\mathrm{Im}(1/\epsilon)$ and $-\mathrm{Im}(1/\epsilon+1)$ for both GaSe and InSe are well in agreement with the LEELS spectra, although the relative intensity of each peak shows minor disagreement between experiment and calculation. This seems to indicate that dielectric theory[32] is applicable to the loss mechanism in these crystals. The peak energies appearing in $-\mathrm{Im}(1/\epsilon)$ and $-\mathrm{Im}(1/\epsilon+1)$ are also shown in Table I.

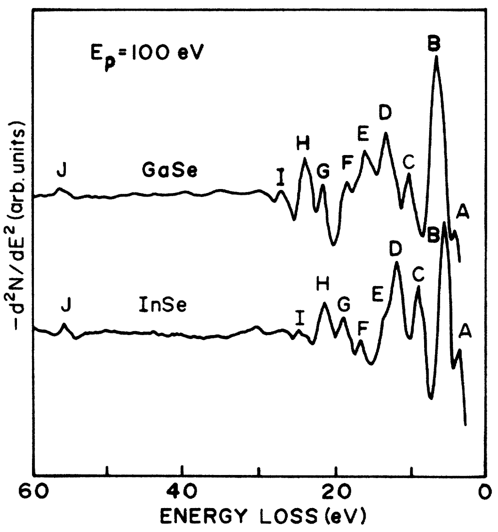

FIG. 1. Second derivative of low-energy electron-loss spectroscopy (LEELS) spectra of GaSe and InSe at a primary electron energy $E_p=100$ eV.

The significant difference between the bulk loss function and the surface loss function is the appearance and disappearance of peaks *D* and *E*. The largest peak *E* in the bulk loss function appears at 16.5 eV for GaSe and 14.5 eV for InSe, respectively. These energies are close to the energies corresponding to $\epsilon_1=0$ for each crystal,[11] where the bulk plasmon is excited. This peak does not exist at all in the surface loss function. In LEELS spectra,

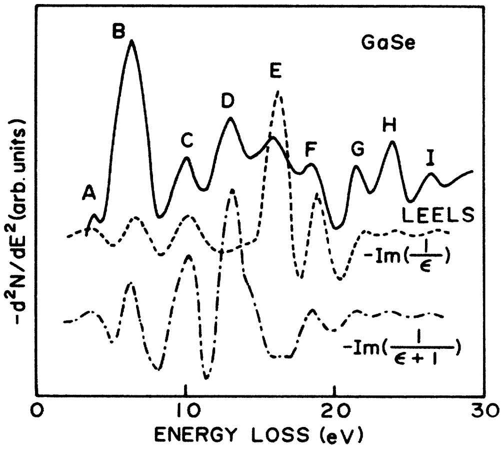

FIG. 2. Comparison of the second derivative of the bulk [$-\mathrm{Im}(1/\epsilon)$] and surface [$-\mathrm{Im}(1/\epsilon+1)$] loss functions calculated from the optical data of Ref. 11 with the experimental LEELS spectrum of GaSe at $E_p=100$ eV.

TABLE I. Peak energies in the LEELS spectrum and the second derivative of loss functions calculated from the optical data (Ref. 11). All energies are in eV. Assignments for each loss peak are also shown.

	GaSe			InSe			
Peak	LEELS	$-\mathrm{Im}(1/\epsilon)$	$-\mathrm{Im}(1/\epsilon+1)$	LEELS	$-\mathrm{Im}(1/\epsilon)$	$-\mathrm{Im}(1/\epsilon+1)$	Assignment
A	3.9	3.6	3.5	3.5	3.5	3.6	$V_1 \rightarrow C_1$
B	6.4	6.7	6.4	5.7	5.8	5.8	$V_3 \rightarrow C_1$[a]
C	10.0	10.5	10.3	9.0	9.2	8.8	$V_4 \rightarrow C_1$[b]
D	13.0		13.2	11.8	12.1	11.6	$\hbar\omega_s$
E	16.0	16.5		13.8	14.5		$\hbar\omega_p$
F	18.6	18.9	18.7	17.0	16.8	15.6	$V_5 \rightarrow C_2$
G	21.4	21.9	21.5	19.3	19.6	20.0	Ga 3*d* (In 4*d*)$\rightarrow C_1$
H	23.8	24.1	23.9	21.4	22.0	21.6	Ga 3*d* (In 4*d*)$\rightarrow C_2$
I	26.4	26.7	26.6	25.6	25.3	25.2	Ga 3*d* (In 4*d*)$\rightarrow C_3$
J	56.4			55.6			Se 3*d*$\rightarrow C_1$

[a] $V_1 \rightarrow C_2$ is also possible.

[b] $V_2 \rightarrow C_3$ is also possible in GaSe.

the energy of this peak is 16.0 eV for GaSe and 13.8 eV for InSe which are close to the energies of peak *E* in $-\mathrm{Im}(1/\epsilon)$ for GaSe and InSe. Peak *E* in LEELS can thus be considered to be due to the bulk-plasmon loss. The observed bulk-plasmon energy of GaSe (16.0 eV) is the same value as the calculated one (16.0 eV), assuming nine oscillating electrons per GaSe molecule, while, in InSe, the observed value (13.8 eV) is a little smaller than the calculated one (14.5 eV). These bulk-plasmon energies are also confirmed by satellite emissions of some core and Auger electrons excited by Mg *Kα* x rays, as shown in Fig. 4. These satellites, indicated by arrows, are apparently due to the bulk-plasmon loss from the main peaks. The energy separation between each main peak and the satellite is about 16.0 eV for GaSe and 14.0 eV for InSe. The bulk-plasmon energies $\hbar\omega_p$ of GaSe and InSe reported in the literatures are shown in Table II. The value of GaSe is around 16 eV in all references, and that of InSe is around 14 eV.

The second derivative of the surface loss function $-\mathrm{Im}(1/\epsilon+1)$ shows a maximum at 13.3 eV for GaSe and 11.6 eV for InSe, as shown in Figs. 2 and 3, respectively. The corresponding peak is not present in the $-\mathrm{Im}(1/\epsilon)$ of GaSe, and is small in that of InSe. This peak is very close to peak *D* in LEELS spectrum for both GaSe (13.0 eV) and InSe (11.8 eV). Furthermore, the value of 11.8 eV for InSe is nearly in agreement with the surface-plasmon energy $\hbar\omega_s = 11.6$ eV for InSe reported by Williams *et al.*[33] They measured the electron energy losses associated with In 4*d* core electrons in InSe excited by Al *Kα* x rays, and obtained values of 14.0 eV and 11.6 eV for $\hbar\omega_p$ and $\hbar\omega_s$, respectively, by observing the angle dependence of the intensity of losses with respect to the surface normal. These results seem to demonstrate that peak *D* is due to excitation of a surface plasmon.

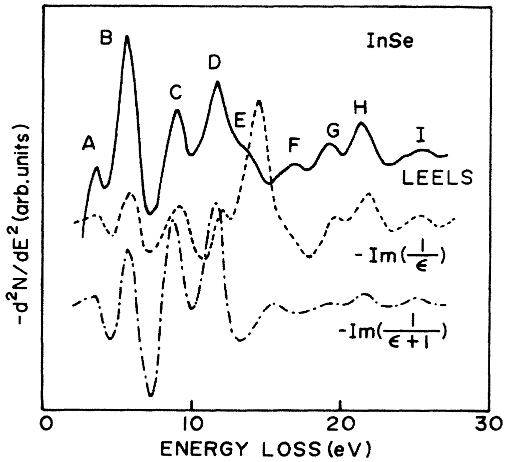

FIG. 3. For explanations see captions of Fig. 2; InSe instead of GaSe.

The surface-related nature of peak *D* is also clear from the primary energy dependence of LEELS spectra of GaSe and InSe, as shown in Figs. 5 and 6, respectively. The primary electron energy was changed from 40 to 160 eV. The energies of each peak are nearly constant, while

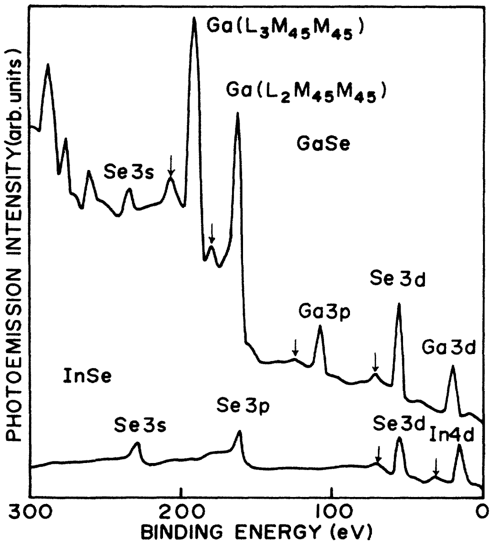

FIG. 4. Bulk-plasmon satellites shown by the arrows of some core and Auger [$\mathrm{Ga}(L_3M_{45}M_{45})$ and $\mathrm{Ga}(L_2M_{45}M_{45})$] lines in XPS spectra of GaSe and InSe.

TABLE II. Bulk- ($\hbar\omega_p$) and surface- ($\hbar\omega_s$) plasmon energies of GaSe and InSe reported in the literature. All energies are in eV.

	GaSe		InSe	
	$\hbar\omega_p$	$\hbar\omega_s$	$\hbar\omega_p$	$\hbar\omega_s$
Present work				
LEELS	16.0	13.0	13.8	11.8
XPS	16.0		14.0	
Williams *et al.*[a]				
XPS			14.0	11.6
Soukiassian *et al.*[b]				
electron energy loss	16.5		14.8	
Mamy *et al.*[c]				
optical	16.0			
Piacentini *et al.*[d]				
optical	16.0		14.0	

[a] Reference 33.
[b] Reference 22.
[c] Reference 10.
[d] Reference 11.

the relative intensities of each peak depend significantly on the primary energy. A detailed comparison of the relative intensities is rather complicated, but it is clear from these figures that the intensity of peak *D* decreases with a decrease in primary energy as compared with other peaks, especially peak *C*. The escape depth of electrons excited in metals and semiconductors exhibits its minimum value of about 5 Å around the kinetic energy of 80—150 eV, while it is about twice as large at ~40 eV as at ~100 eV. Thus, the probing depth is deeper at ~40 eV than at higher energies. Therefore, the decrease in intensity of peak *D* with decrease in primary energy indicates that peak *D* is associated with the surface. The above conclusion that peak *D* is due to the surface-plasmon excitation is thus consistent with this result that the intensity of peak *D* depends on the primary energy.

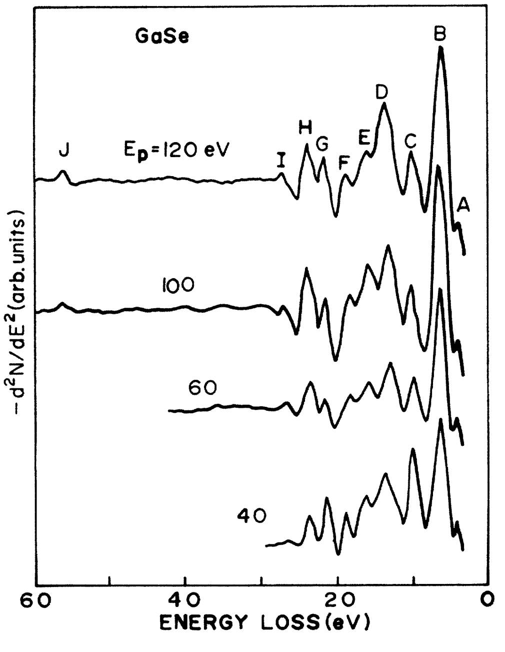

FIG. 5. Primary energy dependence of LEELS spectrum of GaSe.

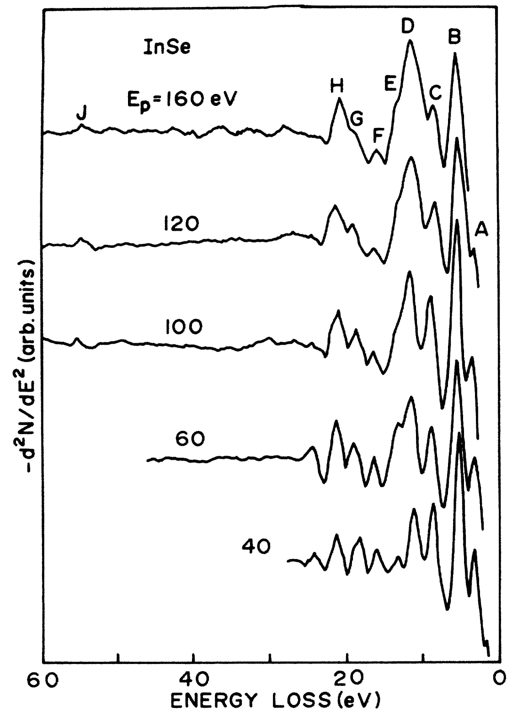

FIG. 6. Primary energy dependence of LEELS spectrum of InSe.

B. Core and valence-band excitations

Except peaks *D* and *E*, all other losses are considered to be one-electron transitions from the core levels and the valence band to empty bands. For the assignment of available transitions to these losses, XPS spectra of the valence band and upper core levels were measured as shown in Figs. 7 and 8 for GaSe and InSe, respectively. The binding energy is relative to the Fermi level. The overall structures of the spectra are well in agreement with the literature.[13,16,18] The emission line around 54.5 eV in both GaSe and InSe corresponds to the excitation of the Se $3d$ core electrons. The lines at 19.7 eV for GaSe and at 18.3 eV for InSe are due to the Ga $3d$ and In $4d$ levels, respectively. The valence band spreads over 0—16 eV, and consists of five structures denoted as V_1-V_5. The peaks labeled α_3 and α_4 are the x-ray ($K\alpha_3$, $K\alpha_4$) satellites of the Ga $3d$ level in GaSe,[13] or the In $4d$ level in InSe. The valence band V_4 in InSe is masked by the satellite α_4. The atomic nature of these valence-band structures is as follows:[7,18] The uppermost structure V_1 consists of the hibridization of the s- and p_z-like orbitals of the metal atoms with the p_z-like orbitals of the chalcogen atoms, and has symmetry Γ_4^- and Γ_1^+ at the Γ point in the Brillouin zone. The next structure V_2 is mainly formed by the chalcogen p_x and p_y orbitals with symmetry Γ_5^-, Γ_6^+, Γ_5^+, and Γ_6^-. The third and fourth structures V_3 and V_4 originate from the metal s-like orbitals; V_3 with symmetry Γ_1^+ and Γ_4^- is the Ga-Ga (or In-In) anti-

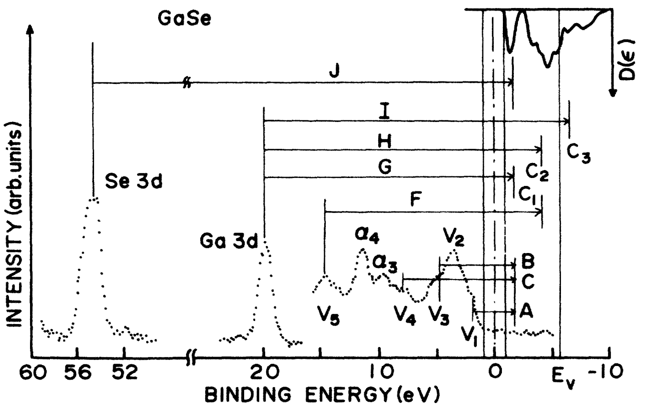

FIG. 7. Assignments of possible transitions for the loss peaks observed in the LEELS spectrum of GaSe combined with XPS spectra of upper core levels and valence band (see also Table I). C_1, C_2, and C_3 represent the final states for transitions from Ga 3d core level. Binding energy is referred to the Fermi level, and the density of states of the conduction band in the upper-right corner of figure is taken from Ref. 11.

bonding band, while V_4 with symmetry Γ_3^+ and Γ_2^- is a bonding band. The lowest band with symmetry Γ_1^+, Γ_4^-, Γ_2^-, and Γ_3^+ is due to the chalcogen Se 4s orbitals.

The density of states of the conduction band calculated by Piacentini *et al.*[11] is also shown in the upper-right corner of Figs. 7 (GaSe) and 8 (InSe). There is an energy gap between the lowest and higher structures of the conduction band for both GaSe and InSe. The higher conduction band has a complicated structure, and spread above and below the vacuum level E_v, where the energy E_v is 5.7 eV for GaSe and 4.5 eV for InSe (Ref. 31) from the Fermi level.

The possible energy transitions for losses observed in LEELS spectra are given by arrows in figures, where the length of the arrow indicates the corresponding energy loss. The energy loss of peak J in GaSe is 56.4 eV. This loss is slightly larger, about 0.4 eV, than the separation (56.0 eV) between the Se 3d level and the peak found in the lowest conduction band, as shown in Fig. 7. This difference in energy for InSe is also small, only ~0.5 eV. Thus, it is clear that peak J originates from the loss due to the transition between the Se 3d level and the lowest conduction band.

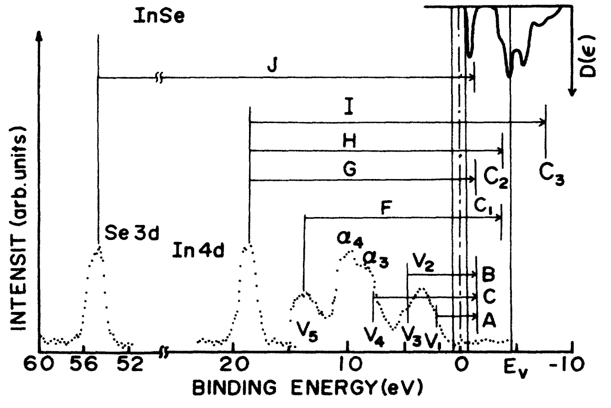

FIG. 8. For explanations see caption of Fig. 7; InSe instead of GaSe.

The structures appearing in $-\mathrm{Im}(1/\epsilon)$ and $-\mathrm{Im}(1/\epsilon+1)$ above 20 eV for GaSe and 18 eV for InSe, as shown in Figs. 2 and 3, come from the Ga 3d—(In 4d—) related structures in the optical data.[11] Therefore, the comparisons shown in Figs. 2 and 3 suggest that peaks G, H, and I in the LEELS spectrum are due to the excitation of Ga 3d electrons in GaSe, and In 4d electrons in InSe. This assignment gives three final states C_1, C_2, and C_3 for transitions from the Ga 3d (In 4d) level, as shown in Figs. 7 and 8. The final state C_1 for peak G coincides with that of peak J. On the other hand, the final states C_2 and C_3 for H and I fall within the upper conduction band. C_2 lies below the vacuum level, while C_3 lies above the vacuum level by about 1 eV in GaSe, and about 3 eV in InSe. We note here that the energy C_3 above the vacuum level is close to one of the peak energies of the density of states of the conduction band above the vacuum level reported by Margaritondo *et al.*:[15] They have obtained several peaks in the density of states of the conduction band above the vacuum level, by observing CIS spectra in the UPS study with synchrotron radiation, in which the energies of lower three peaks are $\underline{0.9}$, 1.5, and 2.1 eV in GaSe, and 1.6, $\underline{3.3}$, and 4.1 eV in InSe, respectively. The underlined energies are well in agreement with the position of C_3 for both GaSe and InSe.

The LEELS spectra due to the transition from upper core levels have been sometimes used to determine the position of empty surface states in the band gap.[26,34] In the present case, we have not observed such transitions, and all final states for the excitation of Ga 3d (In 4d) electrons fall within the conduction-band region. These results seem to demonstrate that there are no empty surface states in these compounds, consistent with the fact that no dangling bonds exist on the cleaved surface.

The energy loss of peak F corresponds to the energy separation between the valence band V_5 and the upper conduction band. It should be noted that the final state for F coincides with that for H shown in the figures marked C_2.

The above assignments for peaks F—J seem to demonstrate that the final states for the excitation of Ga 3d (In 4d) electrons are also to be the final states for the losses A, B, and C. The most likely assignment is to select one final state C_1 for all three losses A, B, and C. In this case, the initial state for A is the valence band V_1, and that for B is V_3, and that for C is V_5, as shown in Figs. 7 (GaSe) and 8 (InSe). However, other assignments are possible for B and C. For example, the energy loss of peak B is also nearly equal to the energy separation between V_1 and C_2, in both GaSe and InSe. The energy loss of peak C in GaSe is also about the same as the separation between V_2 and C_3, while this is not true in InSe. In fact, the peaks A, B, and C appearing in $-\mathrm{Im}(1/\epsilon)$ and $-\mathrm{Im}(1/\epsilon+1)$, shown in Figs. 2 and 3, originate from the complicated structures in the optical data,[11] and the several different assignments have been suggested for these structures.[6,10–12]

C. Ar^+-ion sputtering

Figures 9 and 10 show the effect of Ar^+-ion sputtering on the LEELS spectrum at $E_p=100$ eV of GaSe and InSe, respectively. The uppermost spectrum is that of a freshly cleaved surface, and the lowest one is taken from Ga or In metals, respectively. The bulk- and surface-plasmon peaks in metal are denoted by $\hbar\omega_p$ and $\hbar\omega_s$ in the figures. These energy positions of bulk and surface plasmon coincide with the results for Ga and In thin layers on Si(111) surface reported by Rowe *et al.*[35]

As seen in these figures, the spectrum after 30 min of sputtering becomes very similar to that of pure metal Ga (Fig. 9) or In (Fig. 10), except that peak J originating from Se $3d$ is not present in the spectrum of pure metal. The similarity is especially good for GaSe. Moreover, the loss peaks appear in metal Ga or In are also present in the spectrum from the surface sputtered for 30 min. The most interesting results, in the spectrum of sputtered surface, however, is the presence of bulk- and surface-plasmon losses of the corresponding metal, also noticeable in these figures. These results indicate that the sputtered surface of GaSe or InSe changes to a thin metallic layer of Ga or In, respectively.

Peak A becomes very small with only 5 min of sputtering, and, in GaSe, a new peak related to Ga metal appears near A which grows with further sputtering. Peak B in GaSe remains with about the same energy and intensity even after 30 min, since Ga metal also exhibits large peak at this same energy. In InSe, however, peak B disappears with continued sputtering, and a new structure appears, perhaps corresponding to the structure at about 3.5 eV in In metal. Peaks C, H, and I become smaller with sputtering. Most rapidly, peak C disappears in about 30 sec, since at this energy, there are no peaks in both Ga and In metals. Peak G is replaced by the corresponding peak of the metal for both Ga and In. Peak F quickly shifts to a slightly lower energy in the sputtering, and soon disappears.

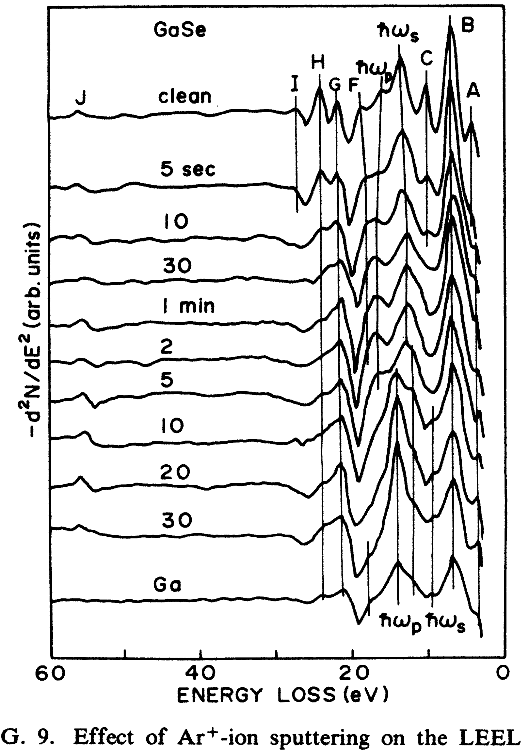

FIG. 9. Effect of Ar^+-ion sputtering on the LEELS spectrum of GaSe at $E_p=100$ eV. The lowest is a spectrum of Ga metal.

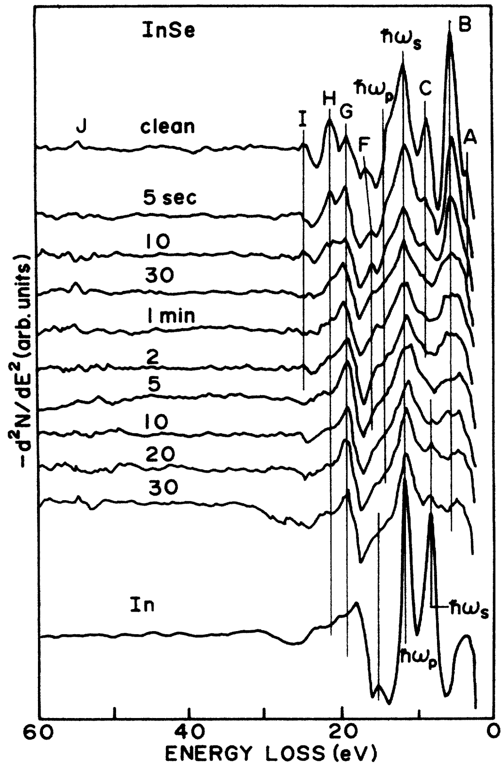

FIG. 10. Effect of Ar^+-ion sputtering on the LEELS spectrum of InSe at $E_p=100$ eV. The lowest is a spectrum of In metal.

The bulk- and surface-plasmon peaks $\hbar\omega_p$ and $\hbar\omega_s$ of the starting materials remain through 5 min of sputtering. However, in GaSe, the spectrum at 10 min is considerably different from the one at 5 min. In the 10-min spectrum, the intensities of $\hbar\omega_p$ and $\hbar\omega_s$ of GaSe decrease, and the bulk and surface plasmons of Ga metal begin to appear, as shown in Fig. 9. Also in InSe, the surface plasmon of In begins to appear at 10-min sputtering, as shown in Fig. 10.

Thus, the surface of GaSe (InSe) begins to behave like a thin layer of metallic Ga (In) after 10 min of Ar^+-ion sputtering under the experimental conditions. The present findings on the metallic nature of sputtered surfaces of GaSe and InSe confirm the previous results obtained by XPS.[29,30]

IV. CONCLUSIONS

LEELS has been applied to the layered semiconductors GaSe and InSe for the first time. Ten loss peaks are observed in the second derivative of the LEELS spectra of both GaSe and InSe. In comparison with the second derivative of the loss functions calculated from optical data, two loss peaks are assigned to excitations of bulk and surface plasmons. XPS spectra of the valence band and some upper core levels have also been measured, which enable us to assign possible transitions for each of the energy losses due to one-electron transitions. The losses due to the excitation of Ga 3*d* (In 4*d*) core electrons yield three final states in the conduction band. Two of these lie below the vacuum level, and one lies above. The other five loss peaks are explained by transitions from the Se 3*d* level and the valence band with final states the same as with Ga 3*d* (In 4*d*) levels.

The spectra after Ar^+-ion sputtered surfaces show bulk- and surface-plasmon losses of metallic Ga in GaSe, and In in InSe. This indicates that the surface of these crystals is changed to a thin metallic layer by Ar^+-ion sputtering.

ACKNOWLEDGMENT

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