Electron Energy-Loss Spectroscopy of GaAs and Ge Surfaces*

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The energy-loss spectra of ~100-eV electrons were measured for (100) and ($\bar{1}\bar{1}\bar{1}$) GaAs and (111) Ge surfaces. The portion of the energy-loss spectra attributed to excitations of d electrons is proportional to the density of states in the conduction bands and empty surface states. The GaAs surfaces stabilized into Ga-rich and As-rich conditions permit unambiguous identification of intrinsic surface states. Empty and filled surface states, attributed to dangling Ga and As bonds, are observed near the conduction-band and valence-band edges, respectively.

We report in this Letter low-energy-loss spectroscopy (LELS) on GaAs and Ge surfaces with special emphasis on $3d$-core-to-conduction-band transitions. These transitions allow the precise probing of *empty* bulk and surface states, in contrast to the more complex spectra involving the excitation of valence electrons. In addition, by stabilizing the polar ($\bar{1}\bar{1}\bar{1}$) and (100) GaAs surfaces to terminate in a surface layer predominantly composed of either As or Ga atoms, we are able to provide a unique and convincing method of characterizing both empty and filled intrinsic surface states.

Because of the absence of a rigorous theoretical treatment, interpretation of the observed LELS spectra is presently somewhat controversial. The energy-loss spectra have been interpreted in terms of a dielectric model[1] and a density-of-states model.[2] In view of the indirect nature of the electronic transitions,[3] which may involve momentum changes comparable to a reciprocal-lattice vector, an interpretation of LELS data in terms of the dielectric loss function at zero wave number seems dubious. An interpretation in terms of a density-of-states model is equally unsubstantiated, except, possibly, under special conditions. It is one of the conclusions of this Letter that such an interpretation may be valid if the energy-loss spectrum arises from electronic transitions from narrow, filled energy levels to empty conduction-band states, provided there is no additional interfering loss channel of comparable energy. We believe this to be true for excitations of d electrons in GaAs and Ge and probably for other materials with narrow isolated d or f core levels.

An approximate expression for the number of electrons suffering an energy loss $\Delta\epsilon$ due to indirect excitations of valence electrons of energy $\epsilon_v(\vec{k})$ to empty conduction-band states of energy $\epsilon_c(\vec{k}+\Delta\vec{k})$ is given by[3]

$$I(\Delta\epsilon)=\sum_{v,c}\sum_{\Delta\vec{k}}F_{v,c}(\vec{k},\Delta\vec{k})\int\frac{d^2k}{\nabla_k[\epsilon_c(\vec{k}+\Delta\vec{k})-\epsilon_v(\vec{k})]_{\epsilon_c-\epsilon_v=\Delta\epsilon}},\tag{1}$$

where $F_{v,c}(\vec{k},\Delta\vec{k})$ is proportional to the scattering cross section. The integral in Eq. (1) is a generalization of the joint density-of-states function for optical interband transitions to include finite momentum changes in the sum over $\Delta\vec{k}$. For a narrow valence band v', $\nabla_k\epsilon_{v'}(\vec{k})\approx 0$. If furthermore this band is isolated and no other scattering channels exist near $\Delta\epsilon$, Eq. (1) may be written as

$$I_{v'}(\Delta\epsilon)\approx\sum_c\bar{F}_{v',c}N_c(\Delta\epsilon),\tag{2}$$

where $\bar{F}_{v',c}$ is the function $F_{v',c}$ averaged over all available $\Delta\vec{k}$, and $N_c(\Delta\epsilon)$ is the density of states of the conduction band c. Thus, except for a possible modulation due to $\bar{F}_{v',c}$, $I_{v'}(\Delta\epsilon)$ is proportional to the conduction-band density of states and includes both bulk and surface features because of the shallow sampling depths (typically $\lesssim 10$ Å). The conditions implied in Eq. (2) seem to be satisfied by the $3d$ core levels of GaAs, Ge, and several other semiconductors.

The energy-loss spectra were measured by an Auger cylindrical-mirror analyzer with integral coaxial electron gun. The primary beam was at normal incidence to the specimen surface. The primary electron energy was varied between 50 and 200 eV, with 100 eV being a good working compromise between resolution (~0.8 eV) and adequate signal intensity. The lack of shifts in energy of the energy-loss structure with varying primary electron energy suggest that diffractive

effects are unimportant. Both first- and second-derivative spectra were measured, the former permitting better resolution,[4] the latter greater accuracy in the energy position of the energy-loss structure.[1] The samples were cleaned by Ar^+ sputtering and annealed. The GaAs $(\bar{1}\bar{1}\bar{1})$ samples were, in addition, overgrown *in situ* by a thin epitaxial GaAs film, by using a molecular-beam technique,[5] which permitted the stabilization of the atomic surface layer into Ga-rich $(\bar{1}\bar{1}\bar{1})$-$\sqrt{19}$ or As-rich $(\bar{1}\bar{1}\bar{1})$-2 surfaces[6] prior to the energy-loss measurements. The surface structures were monitored by grazing-incidence high-energy electron diffraction. This ability to change the "intrinsic" surface conditions, as opposed to extrinsic contamination by foreign impurity atoms, constitutes a novel and inherently more convincing method of probing the surface-sensitive features of binary compound semiconductors.

Figures 1(a)–1(c) show the second-derivative spectra of various GaAs surfaces. Certain features in the spectra are common to all surfaces and are interpreted in terms of bulk behavior. These features include the 3.4- and 5.6-eV structures attributed to bulk valence-band–to–conduction-band transitions,[7] a peak near 8.6 eV of unknown origin, a doublet structure at 21.3 and 23.5 eV due to Ga $3d$-core-level–to–conduction-band transitions, and a peak at 42.4 eV due to similar transitions from the As $3d$ core level. In addition, peaks due to surface- and volume-plasmon losses are observed near 10.2 eV and 16.2, respectively.

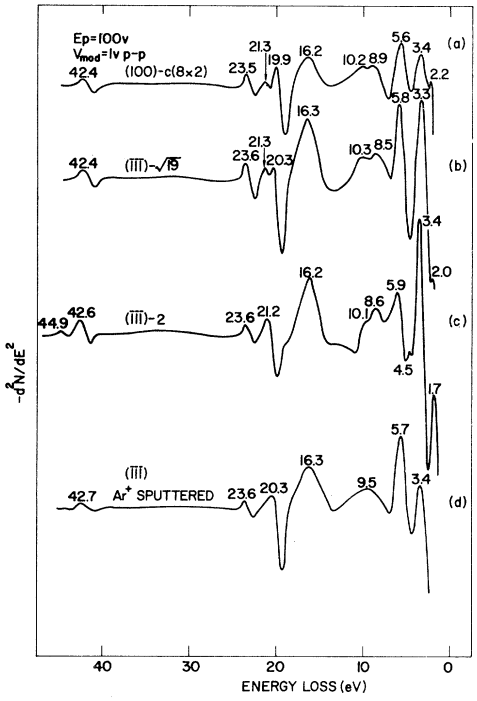

FIG. 1. Second-derivative energy-loss spectra of GaAs: (a) (100) surface, Ga stabilized; (b) $(\bar{1}\bar{1}\bar{1})$ surface, Ga stabilized; (c) $(\bar{1}\bar{1}\bar{1})$ surface, As stabilized; (d) $(\bar{1}\bar{1}\bar{1})$ surface, sputtered.

The energy-loss spectrum of the Ga stabilized (100)-$c(8\times2)$ surface[5] in Fig. 1(a) exhibits surface-sensitive structure at 2.2 and 19.9 eV. We attribute these, respectively, to transitions from the valence band and the Ga $3d$ core level into empty surface states near the bottom of the conduction band arising from dangling Ga bonds at the surface. Ar^+ bombardment enhances these peaks, while oxygen adsorption depresses them.[4]

Stronger evidence for the notion of intrinsic surface states due to dangling bonds is obtained from energy-loss data of the Ga and As stabilized $(\bar{1}\bar{1}\bar{1})$ surfaces shown in Figs. 1(b) and 1(c). The Ga stabilized $(\bar{1}\bar{1}\bar{1})$-$\sqrt{19}$ surface again exhibits structure at 20.3 eV in the region of the d-band transitions. This structure disappears as the surface becomes As stabilized, while a strong peak appears at 1.7 eV, which is attributed to transitions from filled surface states to empty conduction-band states.[8] A small, possibly related structure appears at 4.5 eV which may be due to transitions into higher lying conduction bands. It may also be noted that for the As-stabilized surface a doublet structure is observed in the $3d$-core-level structure of As near 43 eV. The separation of their peaks agrees well with that due to the Ga $3d$-core-level transition. This doublet is not clearly resolved on the Ga-stabilized surfaces because of As depletion in the surface layer. Figure 1(d) shows the loss spectrum of a sputtered $(\bar{1}\bar{1}\bar{1})$ GaAs surface. Sputtering should enhance the density of broken bonds and somewhat deplete the surface of As.[9] This conjecture is supported by the enhancement of the 20.3 eV peak.

Since the energy of the Ga $3d$ core levels with respect to the top of the valence band is quite accurately known for GaAs,[10] it is possible to locate the peaks in the conduction-band density of states with relation to the valence-band edge. This has been done in Fig. 2. The solid curve for the conduction band is obtained from the $3d$-core-level structure of the As stabilized $(\bar{1}\bar{1}\bar{1})$ surface and represents the non-surface-sensitive, or bulk-like, portion of the conduction-band density of states. We have also sketched the estimated position of the filled surface states S_{As} of the $(\bar{1}\bar{1}\bar{1})$-2 structure. Depending on the assumption of the

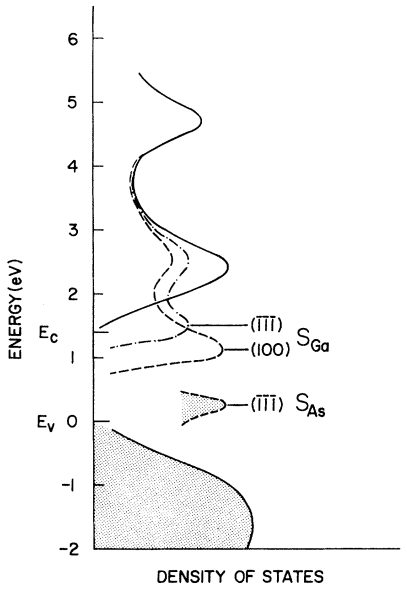

FIG. 2. Conduction-band density of states of GaAs surfaces based on energy-loss spectra of Ga $3d$-core-level excitations: solid line, bulklike density of states for $(\bar{1}\bar{1}\bar{1})$ As-stabilized surface; dot-dashed line, for $(\bar{1}\bar{1}\bar{1})$ Ga stabilized surface; dashed line, for (100) Ga-stabilized surface. S_{Ga} marks the peak positions in the density-of-states curve of empty surface states, and S_{As} that of filled surface states. Energies are referred to the top of the valence band ($E_v = 0$); E_c marks the bulk conduction-band edge.

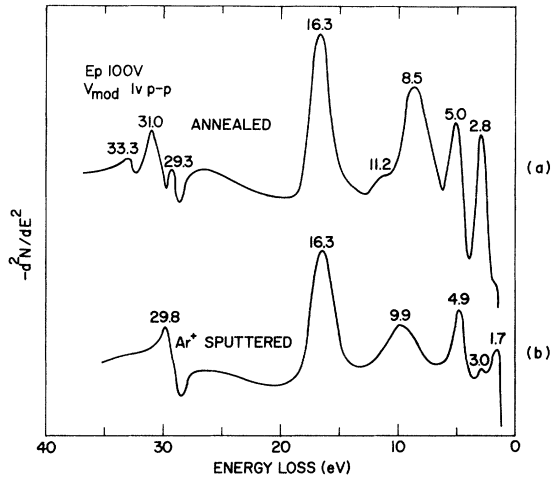

FIG. 3. Second-derivative energy-loss spectra of (111) Ge surfaces: (a) Ar^+ sputtered and annealed; (b) Ar^+ sputtered.

energy position of the final state (possibly the L_1 symmetry point), S_{As} should lie from 0.1 to 0.4 eV above the valence-band maximum. The $(\bar{1}\bar{1}\bar{1})$ S_{Ga} surface state is located near the bottom of the conduction band, whereas (100) S_{Ga} about 0.3 eV below it.

Figure 3 shows preliminary results of the energy-loss spectra of Ge(111) surfaces. The annealed surface [Fig. 3(a)] exhibited a 2×1 surface reconstruction, but because of surface roughness we cannot eliminate the possibility of a 2×8 surface. Again the region of d-core-level transitions near 30 eV is of special interest. The amplitude of the 29.3-eV peak is very sensitive to surface contamination (carbon or oxygen) and may be enhanced and shifted by Ar^+ bombardment, as seen in Fig. 3(b). Ar^+ bombardment also introduces a new structure at 1.7 eV. In analogous manner to GaAs, we interpret these structures as resulting from transitions into empty surface states near the bottom of the conduction band and associated with dangling bonds. The 31.0- and 33.3-eV structures should again correspond to the relative position of peaks in the bulklike conduction-band density of states. The remaining features in the energy-loss spectra of the figure are analogous to those in GaAs.

In summary, the energy-loss spectra due to $3d$-core-level excitations in GaAs, Ge, and related semiconductors gives important information on the relative location in energy of empty surface and conduction-band states. In addition, the ability of stabilizing the surfaces of compound semiconductors by *in situ* molecular-beam evaporation provides a unique method of characterizing both empty and filled intrinsic surface states. This point is particularly important in characterizing noncleaved surfaces of binary compounds, as conventional preparation techniques will leave the surface in a nonstoichiometric and thereby ambiguous condition.

Work is in progress on nonpolar surfaces of GaAs, such as the (110) surface, which contain approximately equal numbers of unsatisfied Ga and As bonds.

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[7]Their energies are somewhat larger than structure expected from direct interband transitions, and are probably related. See, for example, J. R. Chelikowsky and M. L. Cohen, Phys. Rev. Lett. 32, 674 (1974).

[8]Initial experiments on *in situ* As-stabilized surfaces of (100) GaAs also show the suppression of the 19.9-eV surface structure and the appearance of structure at 1.7 eV. A comprehensive report will be published in the future.

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[10]A value of 18.8 eV was obtained both by L. Ley, R. A. Pollak, R. F. McFeely, S. P. Kowalczyk, and D. A. Shirley [Phys. Rev. B 9, 600 (1974)] using x-ray photoemission spectroscopy and by D. E. Eastman (private communication) using ultraviolet photoemission spectroscopy.