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Angle-resolved photoemission studies of Ge(001)-(2×1)

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Ge(001)-(2×1) surfaces prepared by either molecular-beam epitaxy or sputtering followed by annealing were studied with angle-resolved photoemission with use of synchrotron radiation in the photon-energy range of 14—45 eV. The surface electronic structure was found to be independent of preparation procedures. The upper bulk valence-band dispersions of Ge were determined from the Γ point to the X point along the [001] direction in the Brillouin zone; the results are in good agreement with the theoretical band dispersions of Chelikowsky and Cohen [Phys. Rev. B **14**, 556 (1976)]. Three peaks were observed in the normal-emission spectra to show no dispersion over a wide photon-energy range. We will discuss if these peaks are derived from transitions involving surface states.

I. INTRODUCTION

There have been a number of photoemission studies in recent years of the electronic properties of group-IV elemental semiconductor surfaces, including Ge(111)-$c(2\times8)$, Ge(111)-(2×1), Si(111)-(7×7), Si(111)-(2×1), Ge(001)-(2×1), Si(001)-(2×1), etc.[1–10] On many of these surfaces, surface electronic states have been observed and their band dispersions have been determined. The bulk band structure has also been measured in limited regions of $\vec{k}$ space in certain cases. There exist excellent review articles about the theoretical and experimental results on the properties of these surfaces.[1,2]

In this paper we report new angle-resolved photoemission results for Ge(001)-(2×1) taken with photon energies $h\nu=14$—45 eV. This surface was investigated recently by Nelson *et al.*[10] using $h\nu=10$—29 eV. By comparing normal-emission spectra taken with $h\nu=12$, 14, 26, and 27 eV, they identified two peaks at about 0.6 and 1.3 eV below the valence-band maximum (VBM) to be derived from surface states because these two peaks showed no dispersion with respect to $h\nu$ and were contamination sensitive. They also determined parts of the bulk valence-band dispersions along the [001] direction from a set of normal-emission spectra taken with $h\nu=10$—29 eV. Their Ge(001)-(2×1) sample was prepared in the usual manner, that is, sputtering followed by annealing.

Our new data were obtained from surfaces prepared by two different methods: molecular-beam epitaxy[11] (MBE) and sputtering followed by annealing. Since MBE processes are usually performed at lower temperatures than the annealing temperatures for sputtered surfaces, it is interesting to investigate if there is any significant difference in the surface properties of samples prepared by these two methods. For GaAs(001), for example, it is well known that MBE tends to smooth out surface roughness and superior surface quality can be obtained. For Ge(001)-(2×1) we find, however, no significant difference when the photoemission spectra are compared. The spectra presented below were obtained from an MBE-grown surface. The readers can easily verify that our spectra are essentially identical to those reported by Nelson *et al.*[10] in the range of $h\nu=14$—28 eV where the two sets of spectra overlap. The reproducibilty of data by different groups using different sample-preparation procedures is significant in view of the recent controversy concerning the surface-state band dispersions of Ge(111)-(2×1) determined by two different groups.[8,9]

Our wider photon-energy range used allows us to determine the bulk band dispersions in a wider range in $\vec{k}$ space. Using a free-electron approximation for the final-state dispersion,[12,13] we have mapped the upper valence-band dispersions of Ge from the Γ to the X point in the Brillouin zone along the [001] direction. The experimental dispersions are found to be in good agreement with the theoretical results of Chelikowsky and Cohen.[14]

We will show that the two peaks observed with $h\nu\simeq14$ eV near the VBM and identified by Nelson *et al.*[10] as surface-state peaks are in fact predominantly bulk peaks with perhaps some minor contributions from surface-state transitions. We will discuss the question if any of the peaks in the spectra can be unambiguously assigned as being derived from a surface state. This is not a simple question; for example, a "surface state" on Si(111)-(2×1), which had been known for many years, was discovered recently to be actually a feature arising from a bulk transition.[7]

II. EXPERIMENTAL

The photoemission measurements were performed at the Synchrotron Radiation Center of the University of Wisconsin—Madison. Synchrotron radiation from the 240-MeV storage ring Tantalus dispersed by either a Seya monochromator or the newly installed Mark-V Grasshopper monochromator was used as the light source. The photoelectrons were analyzed by a hemispherical analyzer with a 3° full acceptance angle. The overall energy resolution was about 0.15 eV at lower photon energies and about 0.5 eV at higher photon energies. The energy position of the substrate Fermi level was determined by measuring the Fermi-level position of a gold foil in electrical contact with the substrate.

The Ge(001) sample was nominally ultrapure. It was aligned with Laue diffraction to within 1°, mechanically polished to a mirror finish, and chemically etched with dilute NaOCl before insertion into the vacuum chamber. The (2×1) surface was prepared by repeated sputtering and annealing to 600 °C. The sample cleanliness surface atomic order were checked with Auger spectroscopy and high-energy electron diffraction, respectively. During MBE growth, the sample was kept at 500 °C and the evaporation rate was typically about 0.5 Å/sec or less.

The *p*-polarized incident light had an angle of incidence of 60° with respect to the surface normal. The plane containing the incident photon wave vector and the surface normal also contained the [110] axis of the substrate. Thus our photoemission geometry was exactly the same as that used by Nelson *et al.*,[10] facilitating a detailed comparison of the photoemission spectra.

III. RESULTS AND DISCUSSION

A. MBE-grown surfaces versus sputtered and annealed surfaces

Figure 1 shows a set of normal-emission spectra for $h\nu=14$–45 eV obtained from an MBE-grown surface. The binding-energy scale is referred to the Fermi level E_F. The sample surface was determined to be *p* type; the VBM was at about 0.1 eV below the Fermi level.[15] The spectra for $h\nu=14$–28 eV were obtained using the Seya monochromator, while those for $h\nu=30$–45 eV were obtained using the Mark-V Grasshopper monochromator. At 28 eV, the spectra obtained with both monochromators were nearly identical; the only noticeable difference is a somewhat higher secondary electron background for the spectrum obtained using the Mark-V monochromator due to a somewhat larger second-order light leakage. This leakage also generated a noticeable Ge $3d$ core-level peak in the original spectra for $h\nu=30$ and 32 eV just above the VBM, which has been subtracted away in the spectra presented in Fig. 1.

By comparing our spectra shown in Fig. 1 with those reported by Nelson *et al.*[10] for $h\nu=14$–28 eV, one can conclude that the two sets of spectra are essentially identical. The slight difference in background could be due to differences in analyzer transmission functions and spectral purities of the incident light. A few spectra obtained by us on a sputtered and annealed surface are also identical to those shown in Fig. 1 within experimental uncertainties. This observation shows that the surface electronic structure of MBE-grown Ge(001)-(2×1) is the same as that of Ge(001)-(2×1) prepared by sputtering and annealing.

B. Dispersive peaks and bulk valence-band dispersions

There are eight clearly identifiable emission features labeled A–H in Fig. 1; some of which are dispersive as a function of $h\nu$. Feature A arises from the Ge MVV Auger transition and has nearly a constant kinetic energy. The other seven features are derived from photoemission. The assignments of the peaks are facilitated by comparing the present spectra with those for GaAs(001) surfaces reported in Ref. 13; the two systems and related spectra bear many similarities. Referring to Fig. 2, the solid curves are theoretical valence-band dispersions of Ge along the two high-symmetry directions: $\Gamma\Delta X$ or the [001] direction and $\Gamma\Lambda L$ or the [111] direction, which were obtained by Chelikowsky and Cohen using a nonlocal pseudopotential technique.[14] There are altogether four valence bands, labeled 1–4 in Fig. 2; bands 3 and 4 are nearly degenerate and will be referred to as bands 3/4 in the following. In Fig. 2 the binding-energy scale is referred to the VBM at E_V, which is at about 0.1 eV below E_F. Based on the discussion given in Ref. 13, peaks D and F are assigned as direct-transition peaks from bands 2 and 3/4, respectively. The corresponding band dispersions along [001] can be determined directly if we use a free-electron approximation for the final-state band dispersion. This technique of band mapping and the uncertainties in the resulting experimental band dispersions

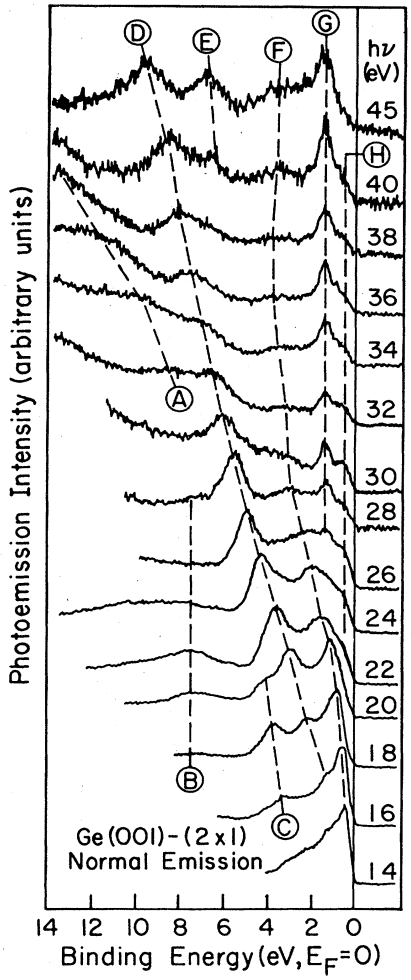

FIG. 1. Normal-emission photoelectron spectra form Ge(001)-(2×1) prepared by MBE. The photon energies $h\nu$ are indicated. The binding-energy scale is referred to the Fermi level E_F. Eight spectral features, labeled A–H, are indicated by dashed lines.

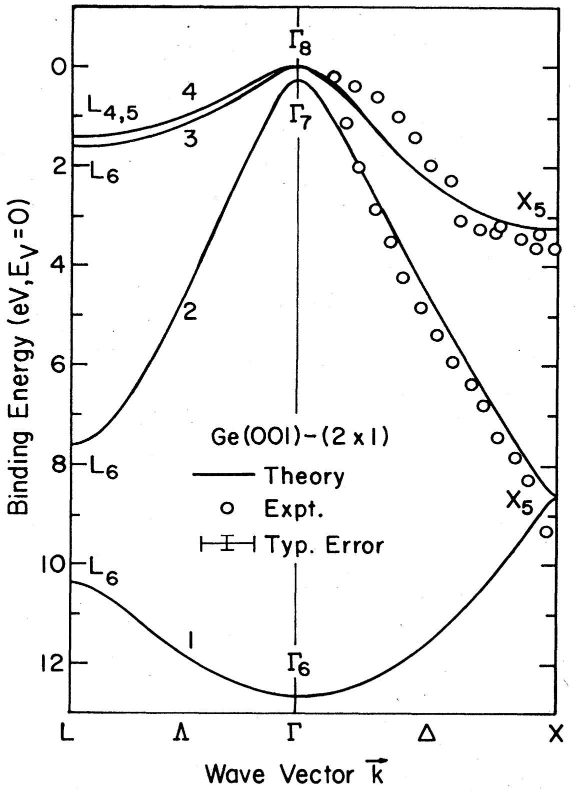

FIG. 2. Experimental (circles) and theoretical (solid curves) dispersions for the four valence bands of Ge along two high symmetry directions $\Gamma\Delta X$ and $\Gamma\Lambda L$ in the Brillouin zone. The critical points are labeled. The binding-energy scale is referred to the VMB at E_V.

have been discussed in Refs. 12 and 13; we will not mention the details here. An inner potential of 7.7 eV is assumed for the free-electron final band of Ge referred to the VBM as in the case of GaAs, because Ge and GaAs have the same lattice constant and same average number of valence electrons per unit volume. The resulting experimental dispersions are shown in Fig. 2 as circles; the estimated typical error is also shown.[12,13] The experimental and theoretical dispersions agree within the estimated error. Nelson *et al.*,[10] using a different technique to map the bands, obtained essentially the same results as ours. Their experimental band dispersions cover a smaller range in the wave vector k because the range of $h\nu$ used is smaller. There are many different techniques for band mapping; we choose the present method because it does not rely on any theoretical final-band calculations.[12,13]

From our data and that of Nelson *et al.*, it is clear that peaks D and F show small but detectable dispersions for $h\nu=10$—16 eV. Their binding energies are small in this range of $h\nu$ because bands 2 and 3/4 near the zone center are probed. Their binding energies happen to be close to those of peaks G and H observed at larger $h\nu$ (see Fig. 1), but the two sets of peaks are not derived from the same transitions. Therefore, peaks D and F for $h\nu=14$ eV cannot be identified as only surface-state emission as done by Nelson *et al.*[10]

Peaks C and E in Fig. 2 are also dispersive and hence must be derived from bulk transitions. Their assignments cannot be certain without accurate knowledge of the final-state band dispersions.[12,13] These peaks will not be discussed further here.

C. Nondispersive peaks and surface states

Features B, G, and H in Fig. 1 are nondispersive as a function of $h\nu$. To judge whether a peak is truly nondispersive, one needs to examine the peak position over a wide range $h\nu$. For example, peak F in Fig. 2 is nearly dispersionless for $h\nu=36$—45 eV; this happens because bands 3/4 are quite flat near the zone boundary. Thus peak F is not a nondispersive peak. Nondispersive peaks in the normal-emission spectra can be derived from either surface states or bulk valence-band critical points with high density of states.[12,13] The distinction between these two possibilities is not necessarily easy.

Peak B has been assigned by Nelson *et al.*[10] to be derived from transitions originating from the second lowest L_6 critical point (see Fig. 2). The (2×1) reconstruction gives rise to a surface reciprocal-lattice vector $(1,1,0)\pi/a$ which can couple, via surface umklapp, the L point in the Brillouin zone with coordinates $(1,1,1)\pi/a$ to an emission direction along the surface normal. The measured binding energy of peak B, about 7.4 eV, is also very close to the theoretical binding energy of 7.6 eV for the second lowest L_6 critical point. By the same argument, peak G with a measured binding energy of 1.3 eV may be associated with the $L_{4,5}$ or L_6 critical points; the theoretical binding energies of $L_{4,5}$ and L_6 are 1.4 and 1.6 eV, respectively, from Ref. 14. Feature H is more like a shoulder than a peak in most spectra. Its binding energy of 0.5 eV is close to the theoretical binding energy, 0.3 eV, of the Γ_7 critical point.[14] But since there is no corresponding feature in the spectra which can be associated with the Γ_8 critical point, it is not likely that feature H is derived from the Γ_7 point. It is possible, however, that feature H is simply a shoulder associated with the rising emission intensity just below the VBM, which can be due to a combination of many emission mechanisms.[12,13] Whether or not features B, G, and H are derived from emission from surface states cannot be clearly decided based solely on their binding energies.

Nelson *et al.*[10] identified features G and H as surface-state peaks based on three reasons: (1) These peaks observed with $h\nu=12$, 14, 26, and 27 eV in their data were dispersionless, (2) these peaks were more sensitive to oxygen contamination than other peaks, and (3) two surface states with similar binding energies had been observed on Si(001)-(2×1).[5] As mentioned above, the two low-binding-energy peaks for $h\nu\simeq 13$ eV identified by Nelson *et al.* as surface-state peaks are in fact predominantly bulk peaks with perhaps some minor contributions from surface-state transitions. Our data to higher $h\nu$ shows convincingly that features G and H are indeed nondispersive. The contamination test is really not a very good quantitative test to distinguish surface and bulk peaks. Because the (2×1) reconstruction is suppressed and surface order is destroyed by oxygen contamination, the bulk-peak intensities can be changed due to surface diffraction or scattering effect, especially in the case of peaks arising from surface umklapp involving surface reconstruction.[12,13] The degree of intensity change associated with contamination depends on many factors and cannot be predicted accurately. Since the atomic and electronic structures of Si(001)-(2×1) and Ge(001)-(2×1) are likely to be similar, it is reasonable to assume that features G and H are derived from surface states with characters similar to those found on Si(001)-(2×1). But this is not a definite proof. It was discovered recently that a surface state on Si(111)-(2×1) known for many years is actually a bulk feature.[7] Thus bulk transitions can sometimes exhibit some characteristics, such as sensitivity to contamination and apparently small dispersions in certain ranges of $h\nu$, which are usually found for surface states.

IV. CONCLUSIONS

We have demonstrated that Ge(001)-(2×1) surfaces prepared by MBE or by sputtering and annealing exhibit identical surface electronic structure. The E-versus-$\vec{k}$ dispersion relations have been determined from the Γ point to the X point in the Brillouin zone along the [001] direction for the upper valence bands. Two features in the normal-emission spectra with constant binding energies of about 0.5 and 1.3 eV relative to the VBM, observed with $h\nu \simeq 26$—45 eV, are very likely derived from surface-state emission, but this cannot be firmly established.

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