

Unoccupied electronic structure of Au and Ag on Ge(111)

B. J. Knapp and J. G. Tobin

Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706

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The surfaces formed by the vapor deposition of Au and Ag on reconstructed $c(2\times 8)\text{Ge}(111)$ were studied with the techniques of k -resolved inverse photoelectron spectroscopy (KRIPES), low-energy electron diffraction, and Auger-electron spectroscopy. Depositions were performed with the samples at room and elevated temperatures. Several interesting structures were observed in the KRIPES spectra, including dispersive peaks and a pair of features that have been assigned as Ag(111)-like intrinsic surface and image-potential states.

In the last ten years metal-semiconductor interfaces have been studied extensively by a number of experimentalists using a vast array of techniques. The adsorption of Ag and Au on Ge(111) is a particularly intriguing case.^{1,2} When deposition of Au or Ag is performed at room temperature on a Ge(111) surface, the growth mode is Frank-van der Merwe with the metal growing in epitaxy.³ However, if the substrate is held at an elevated temperature ($T\cong 300^\circ\text{C}$) then the growth mode proceeds as Stranski-Krastanov.³ Furthermore, a specific geometric structure³ is associated with the elevated temperature depositions; namely $(\sqrt{3}\times\sqrt{3})R30^\circ Z/\text{Ge}(111)$, where $Z=\text{Au}$ or Ag . This $\sqrt{3}\times\sqrt{3}$ structure is irreversibly formed; upon cooling the structure does not revert back to epitaxial growth.¹ Hence, the room-temperature structure could be viewed as a metastable structure. Since many theoretical approaches to surface-adsorbate interactions are based on the minimization of total energy,⁴ it would seem that these $\sqrt{3}\times\sqrt{3}$ structures would be a logical starting point to begin experimentation.

In this paper we report how k -resolved inverse photoelectron spectroscopy (KRIPES) was used to investigate these $\sqrt{3}\times\sqrt{3}$ structures, the clean, reconstructed $c(2\times 8)\text{Ge}(111)$ surface, and the interfaces formed by the room-temperature deposition of Au and Ag on Ge(111). The dispersion of the KRIPES spectral features of the $\sqrt{3}\times\sqrt{3}$ surfaces versus k_{\parallel} is mapped in two high-symmetry directions of the surface Brillouin zone (SBZ). Features related to the bulk Ge(111) crystal are observed in the spectra of the $\sqrt{3}\times\sqrt{3}$ surfaces as well as new dispersive electronic states. In addition, the development of spectral features resembling the intrinsic, unoccupied Ag(111) surface state near E_F and the Ag(111) image-potential state is observed for heavy room-temperature depositions of Ag on Ge(111). To the best of our knowledge this is the first reported observation of an image-potential state of a metal overlayer.

The I_2/CaF_2 Geiger-Müller detector has been employed in these experiments due to its ease of design and operation as well as its sensitivity.⁵ As per other authors, a filling gas such as helium has not been used in the detector.⁶ The detector selects photons of 9.7 ± 0.35 eV due to the onset of photoionization of the I_2 gas and the

transmission cutoff of the CaF_2 window. The electron gun used is based on the design by Stoffel and Johnson;⁷ a low-work-function BaO cathode is utilized that allows the gun to deliver several μA of current at kinetic energies of 5 eV with a beam divergence of several degrees. The cathode is operated at $800\text{--}900^\circ\text{C}$, which gives rise to an energy spread of approximately 0.15 eV. The uncertainty in momentum due to the beam divergence is approximately 0.1 \AA^{-1} . The current striking the sample is integrated during the time of data acquisition so that the spectra can be normalized with respect to charge. The total-energy resolution is essentially determined by the resolution of the detector, which is 0.7 eV (full width at half maximum).

The p -type Ge(111) crystal was cleaned by Ar-ion sputtering and heating to 600°C . Subsequently an anneal was performed at 600°C to induce ordering of the crystal. Auger-electron spectroscopy (AES) was used to determine if contamination was present on the clean or metal-covered surfaces. Only occasionally was any carbon present and then only in quantities that were barely observable above the noise in the AES spectra; the noise-to-Ge(47 eV) ratio is approximately 0.4%. No sign of sulfur or oxygen was ever observed. Low-energy electron diffraction (LEED) was also performed on all surfaces to check for surface ordering. It should be noted that clearly defined eighth-order spots were never observed on the clean, reconstructed Ge(111) surface. Instead, a "cross-like" spot was observed at the position of the half-order spots, indicating that the eighth-order and half-order spots were not being totally resolved. This phenomenon has been observed by other authors, who have worked with Ge(111).⁸ The base pressure in the chamber was approximately 5×10^{-10} Torr or better.

Separate evaporations of Au and Ag were performed from W baskets which were mounted in a shuttered housing which also contained a quartz crystal-thickness monitor. The thickness monitor was calibrated by doing a series of evaporations and checking the growth through the use of AES and LEED. These calibration-curve forms generally agree with the earlier work of Le Lay.³ As demonstrated by Le Lay, a strong break in slope is observed for these curves of Au or Ag AES intensity versus

coverage when the evaporations are performed on a heated substrate. Reportedly, this break in slope corresponds to the completion of the $\sqrt{3}\times\sqrt{3}$ structure and at coverages above the completion of the $\sqrt{3}\times\sqrt{3}$ structure, metal (111) islands begin to form. For the case of Ag on Ge(111), the break in slope was determined to correspond to a coverage of 0.85 Ge(111) ML (ML denotes monolayer);² it is assumed that the coverage at the break in slope for the case of Au on Ge(111) is near this value. Therefore, in all of the KRIPES spectra of the $\sqrt{3}\times\sqrt{3}$ surfaces, coverages that were near the break in slope were used to avoid contributions from the (111) metal islands. However, it should be noted that KRIPES spectra of heavy coverages of Ag on Ge(111) in the $\sqrt{3}\times\sqrt{3}$ structure showed very little difference from those spectra taken from surfaces prepared with coverages near the break

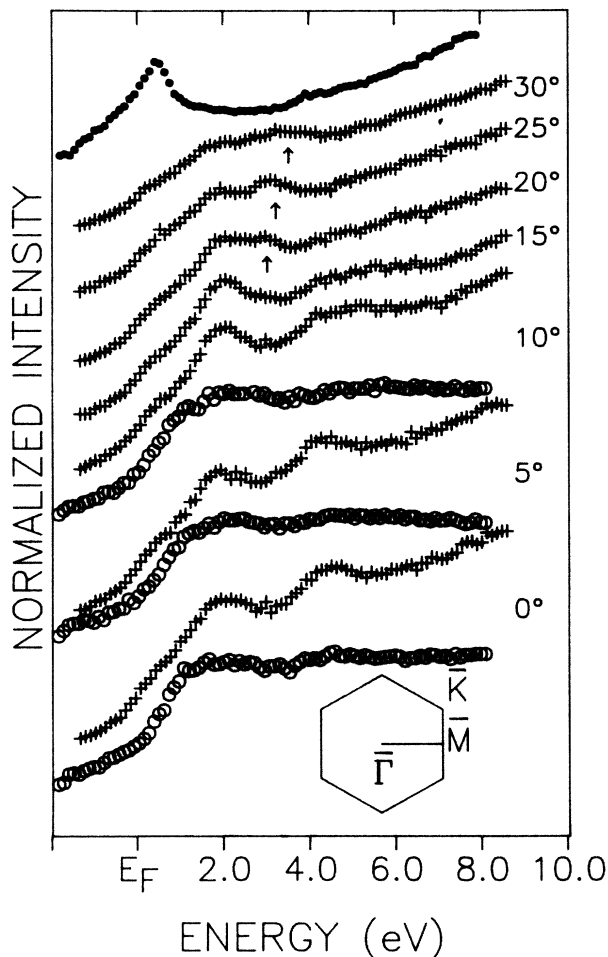


FIG. 1. This figure is composed of KRIPES spectra taken with the electron momentum in the $\bar{\Gamma}$ - \bar{M} azimuthal plane of the 1×1 Ge(111) SBZ. The spectra of clean Ge(111), at angles of incidence (vs the surface normal) of 0° , 5° , and 10° , are plotted using open circles. The $(\sqrt{3}\times\sqrt{3})$ Ag/Ge(111) spectra (pluses) shown here were collected with angles of incidence of 0° , 5° , 10° , 15° , 20° , 25° , and 30° . The top spectrum (solid circles) is a normal-incidence spectrum of >200 ML of Ag deposited onto a room-temperature Ge(111) surface. M and M' have not been distinguished in these experiments (Ref. 10).

in slope. This same situation was observed in photoemission spectra taken on the similar system of Ag/Si(111) by Yokotsuka *et al.*⁹

In Fig. 1, KRIPES spectra of clean $c(2\times 8)$ Ge(111) and Ag/Ge(111) surfaces are shown for various angles of incidence. A full set of clean spectra was collected, but those at larger angles of incidence were not significantly different from those shown here. The clean spectra will be discussed first, then the spectra of the metal-adsorbate surfaces will be examined.

The spectra of clean Ge(111) are dominated by two nondispersive features and one weak, possibly dispersive peak. The most intense nondispersive feature is located at 2.0 eV above the Fermi level. This peak is observed in both azimuths of the SBZ. A similar feature on (2×1) Ge(111) was observed by Straub, Ley, and Himpsel¹⁰ at normal incidence with different photon energies of detection. They noted that this peak did not disperse with k_\perp (momentum perpendicular to the surface) and they deemed it a candidate for a one-dimensional density-of-states (DOS) feature. It would appear from the spectra obtained here that this peak also does not disperse with momentum parallel to the surface and may be a three-dimensional DOS feature. Cohen and Chelikowsky predicted a DOS feature at 2.0 eV above the valence-band maximum in their calculation for bulk Ge(111) (Ref. 11) and it seems reasonable to assign the peak observed in these experiments to that total DOS feature. (It is believed that the Fermi edge and valence-band maximum are at very nearly the same energy for this crystal.¹²)

Another nondispersive peak is seen at 1.0 eV in both azimuths. Straub *et al.* observed a peak near this energy in normal-incidence spectra of cleaved (2×1) Ge(111).¹⁰ They assigned the peak as being due to a surface umklapp to the \bar{M} point of the SBZ. This umklapp, as well as many others, is available on the $c(2\times 8)$ reconstructed surface. When Au or Ag are deposited on the clean surface, this peak is attenuated; this observation may be indicative of the surface nature of this feature. The peak at 4.5 eV is observable in both azimuths near normal incidence. Straub *et al.* also saw a peak near this energy and it is assigned as being due to a transition from a free-electron-like initial state to a bulk-band final state.

When our normal-incidence spectral peak positions, at 1.0, 2.0, and 4.5 eV for clean Ge(111), are mapped onto the experimentally determined band structure of Ref. 10 (Fig. 6 of Ref. 10), excellent agreement exists between the two experiments.

Next, the spectra of the $(\sqrt{3}\times\sqrt{3})$ Ag/Ge(111) and $(\sqrt{3}\times\sqrt{3})$ Au/Ge(111) (not shown) surfaces will be discussed. Several observations can immediately be made, using the $(\sqrt{3}\times\sqrt{3})$ Ag spectra for illustration. [The corresponding $(\sqrt{3}\times\sqrt{3})$ Au and $(\sqrt{3}\times\sqrt{3})$ Ag spectra are qualitatively similar in appearance.] The intensities of the spectral features of the reconstructed, clean surface are generally poorer than for the $\sqrt{3}\times\sqrt{3}$ surfaces. This change in intensities may be due to a reduction of surface umklapping, which, in turn, is due to a reduction of the number of available surface reciprocal-lattice vectors when going from the $c(2\times 8)$ surface to the $\sqrt{3}\times\sqrt{3}$ sur-

faces. A similar observation has been made for the (7×7) surface of Si(111) by Nicholls, Salvan, and Reihl.¹³ The nondispersive peak at 2.0 eV is observable in spectra taken in both high-symmetry azimuths of the $\sqrt{3} \times \sqrt{3}$ surfaces and appears to be bulk-related. The feature that was observed at 1.0 eV in the clean spectra is attenuated and, as mentioned earlier, this may be an indication of the surface nature of this feature. (The residual intensity may be due to a weak Fermi-edge step.) Again there is some intensity around 4.5 eV for the near-normal-incidence spectra and this peak becomes less intense as the crystal is rotated so that the angle of incidence is off normal. It is difficult to determine whether this state is dispersing.

The most interesting feature observed in the $(\sqrt{3} \times \sqrt{3})$ Au or $(\sqrt{3} \times \sqrt{3})$ Ag spectra (Fig. 1) in the $\bar{\Gamma}-\bar{M}$ azimuth of the 1×1 SBZ is a new peak which disperses to increasing energy as the angle of incidence versus the crystal normal is increased, as shown in Fig. 2. When heavy coverages of Ag or Au were deposited on Ge(111) at room temperature, this feature was not observed. This peak appears to be that of a state or resonance of surface or interface character, associated with the $\sqrt{3} \times \sqrt{3}$ structure.

These states may have significant metal p character. A variety of spectroscopic data will be used to support this

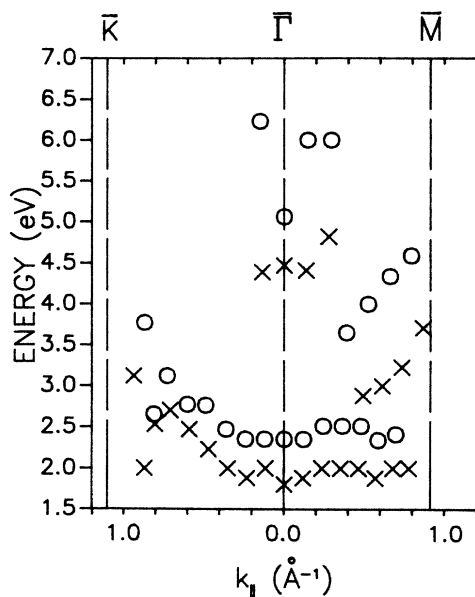


FIG. 2. This figure is a plot of the experimentally observed, unoccupied final-state energies vs the component of electron momentum parallel to the surface (k_{\parallel}) for $(\sqrt{3} \times \sqrt{3})$ Au/Ge(111) (circles) and $(\sqrt{3} \times \sqrt{3})$ Ag/Ge(111) (\times 's), in two high-symmetry directions of the surface Brillouin zone of 1×1 Ge(111). The ordinate scale is energy above the Fermi energy, in eV. Each value of k_{\parallel} was determined by taking the projection of the electron momentum along the surface and assuming conservation of momentum parallel to the surface. For comparison with Fig. 1, note that k_{\parallel} is proportional to the sine of the angle of incidence.

contention. Atomic-absorption experiments of ground-state Ag atoms have found a transition from the $4d^{10}5s^1$ configuration to the $4d^{10}5p^1$ configuration to occur at 4.05 eV.¹⁴ Because of the lack of information about the Ge(111) systems, we will use Ag/Si(111) data to estimate the energy of the occupied sp states. This is justifiable because of the similarity of the temperature-dependent growth modes of Ag/Si(111) and Ag and Au on Ge(111). The occupied sp states on the $(\sqrt{3} \times \sqrt{3})$ Ag/Si(111) system are at approximately 1.0 eV binding energy with respect to the valence-band maximum.¹⁵ Combining the information above, it is estimated that the unoccupied p states should exist near 3 eV above the valence-band maximum. The dispersive states observed on the $\sqrt{3} \times \sqrt{3}$ surfaces in the $\bar{\Gamma}-\bar{M}$ azimuth are at approximately 3 eV above the Fermi energy and it is believed that the Fermi energy and the valence-band maximum agree to within 0.1 eV for this crystal.¹² Thus we infer the possible p character of these $(\sqrt{3} \times \sqrt{3})$ Au and $(\sqrt{3} \times \sqrt{3})$ Ag states. Of course, the above arguments are naively crude and further work is necessary to definitively ascertain the origin of these $\sqrt{3} \times \sqrt{3}$ dispersive states.

The spectra of $(\sqrt{3} \times \sqrt{3})$ Au and $(\sqrt{3} \times \sqrt{3})$ Ag on Ge(111) in the $\bar{\Gamma}-\bar{K}$ azimuth are similar to each other, but different than spectra collected in the $\bar{\Gamma}-\bar{M}$ azimuth. As in the $\bar{\Gamma}-\bar{M}$ azimuth, the bulk-related DOS feature at 2.0 eV is observed and the peak at 1.0 eV, visible on the clean surface, is attenuated. However, in this azimuth there is no clear indication of a dispersing state as in the $\bar{\Gamma}-\bar{M}$ azimuth, but instead the peak at 2.0 eV appears to broaden as the angle of incidence is increased. At the largest angles of incidence it may be possible to identify two peaks, as is indicated in the band mapping of E versus k_{\parallel} in Fig. 2. But it should be mentioned that this assignment of two separate peaks is very weak at best. This broadening and possible two-peak identification is indicative of another dispersing feature, as in the $\bar{\Gamma}-\bar{M}$ azimuth, and again its origin may be partially due to the metal unoccupied p states.

From Fig. 2, it is obvious that the $(\sqrt{3} \times \sqrt{3})$ Au and $(\sqrt{3} \times \sqrt{3})$ Ag band mappings are similar, but with a definite energy shift between the two cases. This shift could be due to several factors. The origin of the effect might be physical: band bending for the two interfaces may be significantly different. It could also be caused by inaccuracy in the measurements. The Fermi edges, as determined from Ta foil in contact with the sample, could have been inaccurately determined. This can arise from variation in the cathode work function due to changing the BaO source and the fact that the detector bandpass is 0.7 eV FWHM. This large bandpass may also contribute to the different dispersions for the features at and above 4.5 eV. These broad peaks become quite weak as the angle of incidence is increased, giving rise to inaccurate energy determinations.

It is interesting to note the strong similarities between the Ge(111) and Si(111) systems. Nicholls *et al.* have obtained KRIPES spectra of $(\sqrt{3} \times \sqrt{3})$ Ag and $(\sqrt{3} \times \sqrt{3})$ Au on Si(111) in the $\bar{\Gamma}-\bar{K}$ azimuth of the 1×1 Si(111) SBZ.¹³ In general, their spectra show qualitative agreement with the spectra presented here and provide

further evidence of the general similarity between all of these $\sqrt{3}\times\sqrt{3}$ noble-metal/elemental semiconductor interfaces.

Some further examples of parallel behavior in Ge(111) and Si(111) will be expounded below. These points will be made within the context of the discussion of room-temperature depositions upon Ge(111). When heavy (> 200 ML) coverages of Ag are deposited onto a room-temperature Ge(111) surface, a Ag(111)-like structure is formed. The LEED patterns resemble those of Ag(111). Moreover, the KRIPES spectra of this surface display a peak near E_F that is very similar to the unoccupied intrinsic surface state of Ag(111), as observed by other investigators.^{16,17} Additionally, a peak corresponding to the image state of this surface was observed if the data were collected over a long period of time to obtain good statistics. These observations run parallel to those for Si(111). Yokotsuka *et al.* observed photoemission spectra that resembled those of Ag(111) for the similar system of Ag/Si(111), when the Ag was deposited at room temperature.⁹

When Au was deposited on a room-temperature Ge(111) crystal, slightly different behavior is observed. The LEED patterns indicated that the surface was not nearly as ordered as the Ag/Ge(111) interface (Le Lay *et al.* have made similar observations¹). Consistent with that, the normal-incidence KRIPES spectra of this Au/Ge(111) surface displayed only a Fermi edge with no spectral structure beyond. The Au(111) KRIPES surface state was not observed.¹⁸ Again, a parallel can be found in the Si(111) system: Nicholls *et al.* saw the same absence of peak structure in the case of KRIPES observations of Au/Si(111), with room-temperature deposition.

The above discussions suggest that ordering has a strong effect on the unoccupied electronic-state structure. An example of this is apparent in Fig. 1. The KRIPES spectrum of the Ag(111)/Ge(111) surface is drastically different than the spectra of the $(\sqrt{3}\times\sqrt{3})$ Ag surface. This trend is seen in all of our data for Au

and Ag on Ge(111) and in the results of Nicholls *et al.* for Au and Ag on Si(111). Normal-incidence spectra of $(\sqrt{3}\times\sqrt{3})$ Ag/Ge(111), $(\sqrt{3}\times\sqrt{3})$ Au/Ge(111), $(\sqrt{3}\times\sqrt{3})$ Ag/Si(111), and $(\sqrt{3}\times\sqrt{3})$ Au/Si(111) all bear a remarkably strong resemblance to each other and are different than the normal-incidence spectra from surfaces formed by room-temperature depositions of Au or Ag on Ge(111). These observations suggest that the unoccupied electronic structures of Au or Ag on Ge(111) or Si(111) are very closely related and are dependent on surface ordering and substrate temperature during deposition.

In summary, we have presented a novel KRIPES, LEED, and AES investigation into the systems composed of Au or Ag on Ge(111). Very strong parallels are observed in the behavior of Au and Ag on Ge(111). These results are also similar to those for these metals on Si(111). The unoccupied electronic structure exhibited strong dependencies upon long-range geometrical ordering, as revealed by LEED, which, in turn, depends on the substrate temperature during evaporations. Dispersive states were observed in the $(\sqrt{3}\times\sqrt{3})$ Ag and $(\sqrt{3}\times\sqrt{3})$ Au surfaces. Deposition of Ag on a room-temperature Ge(111) crystal produced KRIPES spectral features resembling those of the Ag(111) surface, including the image-potential state and intrinsic surface state.

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¹²This information has been gleaned from recently obtained angle-resolved photoemission data. The Fermi energy was determined from spectra of heavy coverages of Au and Ag when deposited on a room-temperature Ge(111) substrate. The valence-band maximum for clean Ge(111) was determined by measuring the energy at which the intensity first rose above the pre-edge level. The difference given in the text of 0.1 eV is a worst case; the value would actually appear to be 20 mV or less. Therefore, for all practical considerations, the valence-band maximum and the Fermi energy can be considered equal.

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