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Studies of the Ag-Ge(100) interface

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The growth mechanism, chemical interaction, crystallographic relationships, and electronic properties of Ag deposited at room temperature on Ge(100)-(2×1) were studied. Nucleation of deposited Ag at about $\frac{1}{3}$ monolayer coverage to form flat and metallic Ag(110) islands was observed with high-energy electron diffraction and photoemission from the valence bands. The growth of Ag at higher coverages was determined to be three dimensional. The $3d$ core levels of surface atoms of Ge(100)-(2×1) did not shift relative to the bulk with Ag coverage of a few monolayers, indicating a very weak interaction between Ag and Ge and negligible intermixing. Annealing experiments showed that the deposited Ag became highly clustered at elevated temperatures and did not wet the Ge(100)-(2×1) surface. We will compare the present results with those for Ag deposited on Ge(111).

I. INTRODUCTION

Despite considerable work in recent years on the research of properties of metal-semiconductor interfaces, many problems and questions still remain.[1] Part of the difficulty may arise as a result of the lack of exact reproducibility in the sample preparation procedures (such as cleaving) and/or insufficient characterization of the systems under study, and therefore, ambiguities often exist in the interpretation of the experimental data. Thus even the seemingly simple question as to the presence or absence of substantial atomic interaction and/or chemical reaction at the metal-semiconductor interface has no clear-cut answer in many instances.

The interfaces made of noble metals deposited on elemental semiconductors such as Ge and Si are expected to be relatively simple compared with interfaces involving compound semiconductors and/or transition-metal overlayers, based on the chemical reactivities of these materials. Many of the noble metal-elemental semiconductor interfaces have been investigated rather extensively before; the major experimental results on the atomic structures and electronic properties were described in a recent review article by Le Lay.[2] The least studied system was Ag-Ge(100). This system as well as Ag-Si and other Ag-Ge interfaces should be particularly simple because no stable Ag-Si or Ag-Ge compounds seem to exist, and therefore, the interface boundaries are likely to be relatively sharp. Indeed, in a recent study of Ag deposited on Si(111) at about 100 °C we found that a Ag overlayer just a few atomic layers thick was essentially indistinguishable from single-crystal Ag(111) in the measured bulk and surface electronic properties, indicating no or negligible mixing of Si into Ag.[3] The purpose of this paper is to provide a clear-cut picture of the interface structure of Ag deposited on Ge(100)-(2×1) at room temperature. We report results from photoemission and high-energy electron diffraction (HEED) measurements. To the best of our knowledge, there is only one other detailed study of this system, by Lince *et al.*,[4] using low-energy electron diffraction (LEED), Auger spectroscopy, and scanning electron microscopy. Some of the present results have been submitted for publication previously in the form of a short paper.[5] Here, we will present a more detailed discussion of the measurements of photoemission line intensities and line shapes for the Ge $3d$ core levels and Ag $4d$ valence levels as well as the HEED patterns as a function of Ag coverage. From the information about the atomic structure (HEED results) and the electronic properties (photoemission results) we provide strong evidence that the Ag-Ge(100) interface is abrupt with no detectable intermixing. The deposited Ag nucleates[6] at about $\frac{1}{3}$ monolayer (ML) coverage and exhibits the (110) face in two domains; the subsequent growth is three dimensional. We will compare our present results with those for Ag-GaAs(100) which is expected to behave quite similarly (even the lattice constants of Ge and GaAs are almost identical).[7]

Our HEED observation regarding the initial growth of Ag seems to be different from that by Lince *et al.*[4] using LEED [nucleation to form Ag(110) at submonolayer coverages versus the observation of an apparent Ge(100)-(1×1)-like pattern]. Furthermore, in a recent study of Ag-Ge(111) interfaces prepared at room temperature Rossi *et al.*[8] explained their results in terms of a model in which a strong chemical interaction took place at the interface resulting in a complex interface with a narrow intermixed region two or three layers thick, and almost pure Ag islands grown on top of it. Since our results indicate that the Ag-Ge(100) interaction is rather weak, an explanation is necessary for the quite different conclusions reached for Ag-Ge(100) and Ag-Ge(111). We will discuss the discrepancies and possible explanations. Such a discussion might also be useful to the explanation of discrepancies found in results for other interface systems.

II. EXPERIMENTAL

Photoemission measurements were performed at the 240-MeV electron-storage-ring Tantalus at the Synchrotron Radiation Center of the University of Wisconsin—Madison using a photoemission chamber with a base pressure of about 10^{-10} Torr. Photon energies were selected to enhance surface or bulk spectral contributions using a 3-m toroidal-grating monochromator.[9] Photoelectrons emitted from the sample were energy analyzed by a double-pass cylindrical-mirror analyzer operated with a pass energy of 5 or 10 eV. Photoelectron count rates were in the range of 10^3 to 10^5 counts/sec typically. The photoemission chamber was also equipped with a HEED system for *in situ* investigation of the sample surface structure.

A nominally ultrapure (undoped) Ge single crystal was oriented to within 1° of a (100) plane by Laue back-diffraction and mechanically ground and polished with this alignment. A clean Ge(100)-(2×1) surface was obtained through repeated cycles of Ar-ion bombardment at 500 eV followed by annealing to about 450 °C. The principal contaminant seen during this process was carbon; cycles were repeated until a carbon-free surface remained after annealing as evidenced by Auger spectroscopy. Our carbon detection limit was estimated to be about 0.02 monolayer. At this point HEED patterns for the sample displayed sharp (2×1) diffraction streaks with good contrast, indicating a smooth Ge(100)-(2×1) reconstructed surface. Carbon contamination would reappear several hours after a clean surface was prepared; new surfaces were generated by additional sputter and anneal cycles as needed throughout the photoemission experiments.

Ag was evaporated from a small Ta boat. The deposit thickness was determined using a quartz-crystal monitor; for the small coverages this monitor was used to determine rates of evaporation through long and repeated timings. Once calibrated the thickness was established by controlling the length of time the shutter was open. It is estimated that these determinations may be in error by as much as 20% for the lower coverages and less for the higher coverages; however, the conclusions of this paper are based on repeated experiments with many different films. All depositions were performed with the sample near room temperature. The chamber pressure during evaporation rose to the 10^{-9}-Torr range and dropped back to the 10^{-10}-Torr range after the evaporator was shut off. Twelve roughly exponentially increasing coverages from 0.01 to 40 Å were examined with photoemission and HEED. Since we determined the Ag growth to be in (110) planes, references to Ag coverage in this paper are also made in terms of equivalent Ag(110) monolayers. These are spaced 1.45 Å apart in bulk Ag. We also point out that since the development of the Ag overlayers is by nucleation and subsequent three-dimensional growth, this expression reflects the average deposit thickness over the sample surface. In these terms, coverages ranged from 0.007 to 27.5 ML in these experiments. The Ge sample position during Ag evaporation was different from that during the subsequent photoemission measurements. An effort was made to reproduce the sample position each time in order to compare the photoemission intensities for different Ag coverages. We tested the precision of our intensity measurements by repeating the same measurement for different Ag films with the same Ag coverage several times, and found that an uncertainty of about 20% in intensity was typical. This uncertainty was mainly derived from irreproducibility of the sample position due to mechanical play of our long-travel manipulator. The measured spectra shapes were, however, quite reproducible because the angle-integrated geometry was not sensitive to this effect.

HEED was used to examine all Ag films prepared for photoemission. Many additional films, including different coverages than these, were prepared for examination by HEED in another ultrahigh vacuum chamber located at the University of Illinois. The same Ge sample was used for these additional measurements. In addition, a Ge molecular-beam source heated with an electron beam was used to grow Ge epitaxial overlayers on the Ge sample at about 400 °C. HEED results on Ag films deposited on the sputtered and annealed Ge surface and the Ge surfaces grown by molecular-beam epitaxy were identical within experimental accuracies. The nucleation of Ag on Ge(100) was reproducibly observed many times.

III. RESULTS

A. HEED studies

Some typical HEED patterns are shown in Fig. 1. Figure 1(a) is the pattern observed for clean Ge(100)-(2×1) with the incident electron beam approximately along the Ge[011] azimuth. The half-order streaks due to the (2×1) reconstruction are almost as intense as the integral-order ones. The spots lying on the middle and lower arcs are diffraction spots from higher Laue zones. The spots on the middle arc are all half-order spots, while the spots on the lower arc correspond to both the integral- and half-order spots. The pattern observed with the electron beam along the perpendicular azimuth, Ge$[0\bar{1}1]$, is identical to Fig. 1(a) because of the two possible orientations of the (2×1) domains oriented at 90° apart.[10] The domained structures of Ge and Si surfaces are quite common; only the cleaved (111) surfaces sometimes show single-domain structures over a macroscopic scale. Of course, the (100) face of Ge cannot be obtained by cleavage.

With increasing Ag coverages on Ge(100)-(2×1) up to about 0.5 Å ($\frac{1}{3}$ ML), the entire Ge(100)-(2×1) pattern is seen to fade somewhat but remains sharp. Beyond $\frac{1}{3}$ ML coverage, additional diffraction streaks corresponding to Ag(110) appear abruptly, indicating that nucleation of Ag occurs at this coverage. This behavior has been firmly established by repeated measurements with very fine steps in increasing Ag coverages.[11] The Ag after nucleation displays domains with two orientations 90° apart; the Ag(110) domains are oriented with the [001] direction parallel to the Ge[011] or $[0\bar{1}1]$ direction. The crystallographic relationship between the Ag domain in one orientation and the top atomic layer of Ge(100), unreconstructed due to Ag coverage (see below), is shown schematically

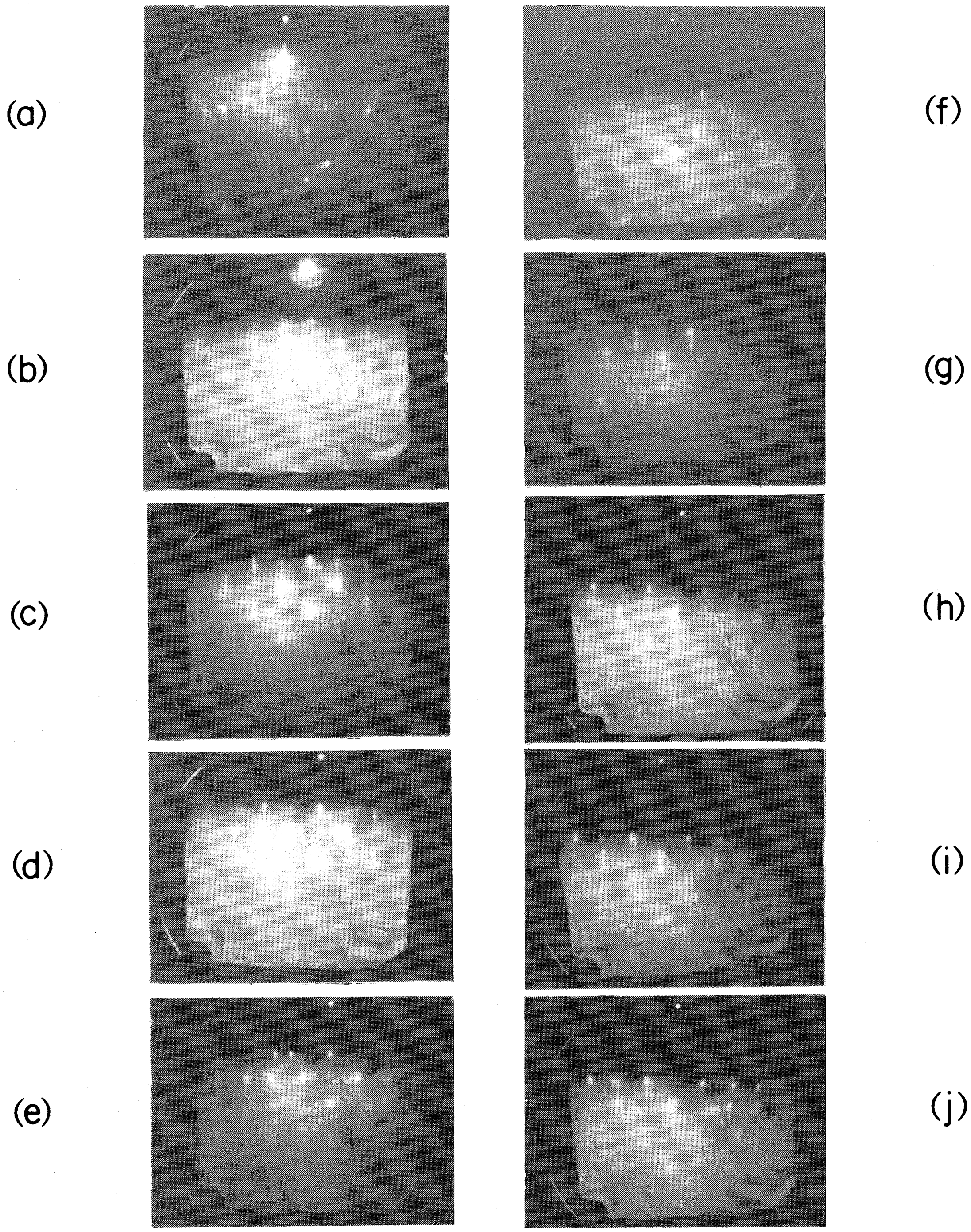

FIG. 1. HEED patterns for (a) clean Ge(100)-(2×1) and (b)—(j) the same surface covered with Ag. The patterns on the left and right are with the incident electron beam aligned approximately with the Ge[011] and Ge[0$\bar{1}$1] directions, respectively. The Ag coverages are as follows: (b) and (f) 2 Å; (g) 5 Å, (c) and (h) 10 Å; (d) and (i) 20 Å; (e) and (j) 40 Å. The electron-beam energy was 8 keV. Some pictures were overexposed in order to show some relatively faint diffraction streaks.

in Fig. 2. Because the lattice constant of Ge is approximately $\sqrt{2}$ times as large as that of Ag, the atomic arrangment shown in Fig. 2 is approximately lattice matched (within about 2%) along the Ag[001] direction.

Just beyond the nucleation threshold, the Ag(110) diffraction pattern and the Ge(100)-(2×1) pattern coexist with full fourfold symmetry. The streakiness and sharpness of the Ag(110) pattern indicate that two-dimensional islands are formed with average lateral dimensions of at least 30 Å. As more Ag is deposited, the half-order streaks from the Ge substrate disappear completely at about 1 Å coverage, but the integral-order streaks are still

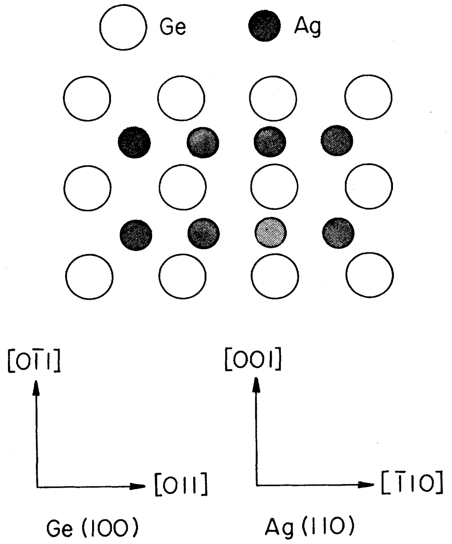

FIG. 2. A schematic drawing to show the crystallographic relationship between the Ge(100) surface atomic plane (unreconstructed due to Ag coverage) and a Ag(110) monolayer. The open and cross-hatched circles represent Ge and Ag atoms, respectively. The crystal directions are indicated. The two lattices are nearly matched along Ag[001].

quite visible. Thus the (2×1) reconstruction of Ge(100) is suppressed at this coverage. Figures 1(b) and 1(f) show the diffraction patterns for 2 Å (1.4 ML) Ag coverage with the electron beam along the Ge[011] and [0$\bar{1}$1] directions, respectively. The bright spots on a circular arc are integral diffraction spots from the Ge substrate; the long streaks are derived from the Ag(110) overlayer with a corresponding lattice spacing of 2.89 Å along the [$\bar{1}$10] direction. The diffraction streaks of Ag islands corresponding to the lattice spacing of 4.09 Å along the perpendicular Ag[001] direction (see Fig. 2) are very weak and cannot be seen clearly in Figs. 1(b) and 1(f). This is interpreted as being due to elongation of the Ag islands in the Ag[$\bar{1}$10] direction.[7] This observation is further confirmed by measurements of streak widths and intensities in the HEED patterns obtained with the electron beam directed at other azimuthal directions.

Figures 1(c)—1(e) show the diffraction patterns with the electron beam along the Ge[011] direction for Ag coverages of 10, 20, and 40 Å, respectively. Figures 1(g)—1(j) are patterns with the electron beam along the Ge[0$\bar{1}$1] direction for Ag coverages of 5, 10, 20, and 40 Å, respectively. As Ag coverage is increased, the pattern still corresponds to Ag(110). The development of diamond-shaped diffraction spots for Ag coverages more than a few ML indicates the formation of three-dimensional structures, that is, the resulting Ag film is rough.

The growth of Ag on Ge at room temperature thus proceeds via nucleation with subsequent three-dimensional growth. This behavior is nearly identical to that observed for Ag on GaAs(100).[7] The nucleation occurs at a Ag coverage of about 0.5 Å for both systems. This is perhaps not surprising because Ge and GaAs have very similar properties and nearly identical lattice constants.

HEED was also used to examine Ag films during and after annealing. While heating Ag films to about 400 °C, a sudden sharpening of the diffraction pattern was observed. Upon cooling to room temperature the Ge(2×1)-reconstructed pattern was again clearly visible, along with very sharp but dotty diffraction lines indicating highly three-dimensional Ag structures containing (110) and (100) faces. Evidently, annealing this system resulted in large areas of the Ge becoming uncovered, the Ag atoms being highly clustered. This result implies that the bonding between Ag and Ge is weak, and Ag does not wet Ge(100) at elevated temperatures.

B. Core-level studies

Chemical reactions between the growing Ag film and the Ge substrate would be expected to induce chemical shifts in the binding energies of the Ag and Ge core levels.[1] The Tantalus ring does not produce usable flux at the energies required to excite the Ag cores, so only the Ge $3d$ levels at about 30-eV binding energy were studied. Both bulk- and surface-sensitive spectra were obtained at 38- and 70-eV photon energies, respectively, for clean and Ag-covered Ge(100)-(2×1).[12] Excellent signal-to-noise ratio was available for all core spectra up to about 5 Å (3.4 ML) Ag coverage. The total instrumental-energy resolution of these spectra was about 0.30 eV as determined from the observed width of the Fermi levels of Ag deposited on the sample holder.

The surface-sensitive Ge $3d$ core-level line shape is a sensitive measure of the degree of interaction between Ag and Ge at the interface. For clean Ge(100)-(2×1), the line shape includes a component due to emission from surface atoms which is shifted 0.41 eV towards lower binding energies relative to the bulk, due to the different bonding of the surface atoms.[12] In this experiment, the surface-sensitive Ge lines show no detectable change in shape from the clean case with increasing Ag coverage to 3.4 ML. Not only are there no extraneous features or shifted components, but the surface-shifted component characteristic of the clean (2×1) surface remains evident. Figure 3 shows surface-sensitive Ge $3d$ core spectra for clean Ge(100)-(2×1) (circles) and one covered with 2 Å (1.4 ML) Ag (crosses). The solid curve is from a least-squares fit to the clean spectrum used previously to determine the surface shift; the model function has been described elsewhere.[12] The long- and short-dashed curves in Fig. 3 indicate the bulk and surface contributions to the core-level spectrum for clean Ge(100)-(2×1). The fit between the clean and Ag-covered spectra and each to the fitted curve is quite good, suggesting a minimum of interaction of the Ag with the surface. Certainly no strong chemical reaction has taken place. The continued presence of the surface-shifted component with Ag coverage and the fact that the (2×1) reconstruction is already suppressed at this Ag coverage indicate that the intrinsic-surface core-level shift for Ge(100)-(2×1) is probably not sensitive to the (2×1) reconstruction which involves perhaps only distortions in the registry of the first few atomic layers from the unreconstructed configuration. The vacancy models[10] for the (2×1) reconstruction in which alternate rows of surface atoms are missing cannot explain the

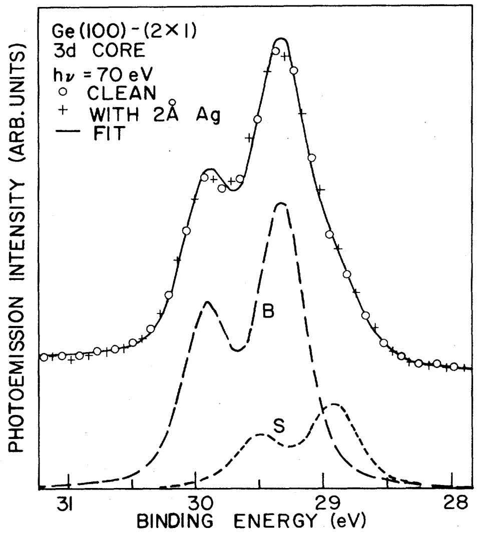

FIG. 3. Surface-sensitive photoemission spectra of the Ge $3d$ core levels taken with $h\nu = 70$ eV. Circles are data for the clean Ge(100)-(2×1) surface while crosses are for the surface covered with 2 Å (1.4 ML) Ag. The two spectra have been normalized to the same area. Binding energies are referred to the valence-band maximum. The solid curve is a least-squares fit to the clean spectrum; the long- and short-dashed curves (displaced vertically for clarity) show the contributions from the bulk (B) and surface (S) of Ge, respectively.

present result easily, because to suppress the reconstruction the surface atoms have to be substantially rearranged, and changes in surface-core-level energies are expected as a function of Ag coverage. The present results are quite similar to those for Ag deposited on GaAs(100) at room temperature,[7] for which both the Ga and As $3d$ surface core levels show only very small changes in energy with Ag coverage.

The photoemission intensities of the Ge core levels decrease with increasing Ag coverage. However, the decrease in intensity of the surface-sensitive spectra is much slower than what one would expect from attenuation by uniform overlayers. Figure 4 shows the normalized integrated intensity of the $3d$ core levels as a function of Ag coverage (circles). The dashed line represents the expected exponential decrease assuming laminar growth and an electron escape depth of 5 Å appropriate for this energy.[13] Significant emission can be seen even at the highest coverage used (40 Å). On the basis of uniform-layer attenuation practically no intensity (less than 4×10^{-4} of the original intensity) would be expected for such a thick layer coverage. These observations suggest either an uneven growth, leaving areas with less coverage and allowing emission from the Ge surface to come out, or mixing of Ge into the Ag overlayers. Both possibilities have been suggested for the case of Ag on Ge(111) surfaces[8] which display similar attenuation behavior; however, in view of the lack of any core-level distortions, mixing is unlikely to be the cause in the present case. Nonlaminar growth, evidenced by HEED measurements, is definitely a cause for this behavior.

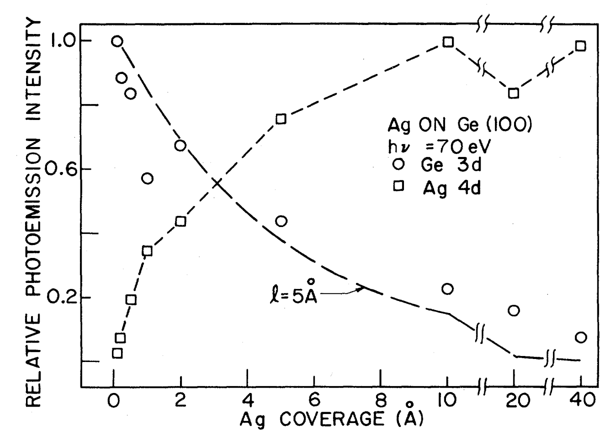

FIG. 4. Relative photoemission intensities (normalized integrated area) for the Ge $3d$ core levels (circles) and the Ag $4d$ levels (squares) as a function of Ag coverage, taken from surface-sensitive ($h\nu = 70$ eV) spectra. The long-dashed curve shows the expected decrease in intensity of the Ge $3d$ core levels assuming attenuation by uniform Ag layers and with an electron-escape depth $l = 5$ Å. The short-dashed curve connects the squares. The experimental uncertainty in intensity is about 20%.

C. Valence-band studies

Figure 5 shows angle-integrated photoemission spectra for Ge and Ag valence bands at all Ag coverages used in the photoemission experiments. The photon energy used was 70 eV, so these curves contain a significant fraction

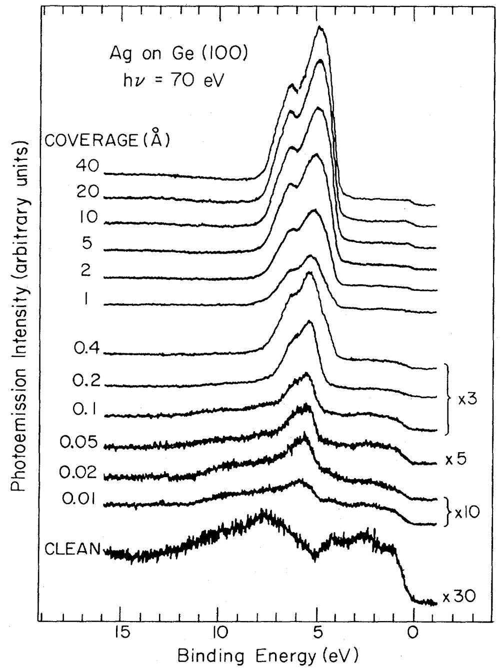

FIG. 5. Valence-band spectra for clean Ge(100-(2×1) and for surfaces with increasing Ag coverage at $h\nu = 70$ eV. Curves are displaced vertically by arbitrary amounts for clarity. Curves for lower Ag coverages are amplified by the indicated factors. The energy scale is referred to the Fermi level.

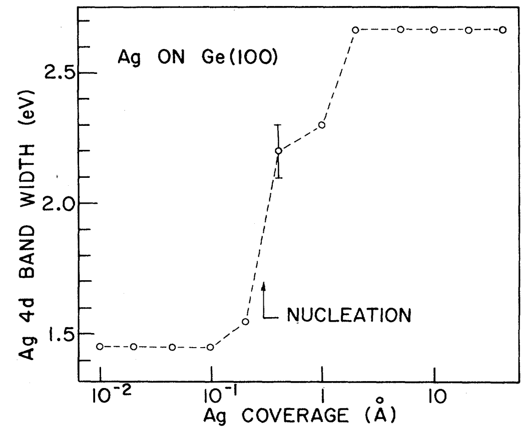

FIG. 6. The full width at half maximum of the Ag 4*d* band (see Fig. 5) with estimated background subtracted as a function of Ag coverage.

of emission from the surface layers. The Ag 4*d*-derived bands are visible at the lowest coverage (0.01 Å) as a small peak superimposed on the Ge valence bands. This peak grows in intensity and widens with increasing Ag coverage. The relative integrated intensity of this Ag 4*d* peak with estimated background substracted is shown in Fig. 4 (squares) as a function of Ag coverage. Because the uncertainty in the intensity measurement is relatively large (about 20%), we cannot use this data to distinguish different growth modes. The increase in width of the Ag 4*d* peak is related to the 4*d*-band formation; at the highest coverage (40 Å) and 4*d* peak looks essentially the same as that for bulk Ag. The full width at half maximum of the Ag 4*d* peak is plotted in Fig. 6 as a function of Ag coverage. The abrupt increase in width around $\frac{1}{3}$ ML Ag coverage is another indication of the nucleation of Ag, in agreement with HEED measurements.

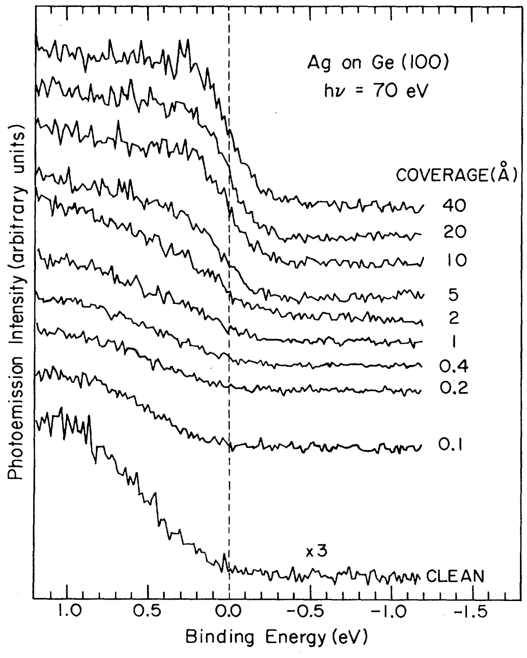

FIG. 7. Magnified photoemission spectra (from Fig. 5) in the vicinity of the Fermi level. The zero of the energy scale is set to the Fermi level indicated by the dashed line.

After nucleation, the Ag islands are sufficiently flat and large to show the Ag(110) diffraction pattern. To investigate if the Ag islands are metallic (i.e., there is a sufficiently high density of states at the Fermi edge), we show in Fig. 7 the magnified valence-band spectra near the Fermi edge for different Ag coverages. The Fermi edge is well developed for the higher coverages, and its location is indicated by the dashed line. The clean spectrum shows that the valence-band maximum of the Ge substrate, which can be quite accurately located by linear extrapolating the leading slope, is at about 0.1 eV below the Fermi edge. Significant emission from states at the Fermi level can be seen in Fig. 7 for Ag coverages of 0.4 Å and greater, consistent with the picture that the Ag islands formed after nucleation are metallic.[14] From core-level measurements, the Fermi level remains at about 0.1 eV above the Ge valence-band maximum for Ag coverages up to a few ML.

IV. DISCUSSION

We will summarize our major results first before discussing the comparisons with other authors' results on related systems.

Ag deposited on Ge(100)-(2×1) at room temperature is dispersed for coverages less than about $\frac{1}{3}$ monolayer. A sharp nucleation process occurs at a Ag coverage of about $\frac{1}{3}$ monolayer and relatively flat, elongated, and metallic Ag(110) islands are formed; the covered part of the Ge surface and immediate vicinity become (1×1), while the rest of the surface is still (2×1). As more Ag is deposited, the (2×1) reconstruction of Ge becomes totally suppressed at about 1-Å coverage, and the Ag growth is three dimensional. From core-level studies and HEED studies of films before and after annealing, one can conclude that the Ag-Ge interaction is very weak and there is no evidence of any strong chemical reaction or intermixing. All experimental results are consistent with an abrupt interface. The clean Ge surface is *p* type and the valence-band maximum remains at about 0.1 eV below the Fermi level for several layers of Ag coverage. The clean Ge(100)-(2×1) surface is most likely derived from the (1×1)-unreconstructed surface by distortions in the registry of the first few atomic layers such that chains or dimers are formed on the surface.[10] As Ag is deposited, the reconstruction is suppressed but the surface core-level energies are not changed. The vacancy models for Ge(100)-(2×1) are most probably not correct. The results for Ag on Ge(100) are extremely similar to those for Ag on GaAs(100).[7] Ag-GaAs(100) is also an abrupt interface displaying nearly identical growth details. The major difference is in the Fermi-level positions; the final Fermi-level position of Ag-GaAs(100) is near midgap and depends somewhat on the starting surface reconstructions. We have no good theories to explain the Fermi-level positions for all these surfaces; this Schottky barrier problem is well known and has not been solved completely.

Results of our observation of the Ag-film growth are in substantial agreement with the low-energy electron-diffraction results of Lince *et al.*[4] who also observed three-dimensional growth of Ag(110) at coverages of more than a couple of monolayers. However, they reported a Ge(100)-(1×1)-like pattern for about 1 ML of Ag on Ge(100). We repeatedly observed submonolayer nucleation with the coexistence of Ge(100)-(2×1) pattern and the Ag(110) pattern just beyond about $\frac{1}{3}$ monolayer of Ag coverage for Ge surfaces prepared by molecular-beam epitaxy and for Ge surfaces prepared by sputtering and annealing. A probable explanation for this difference is that the Ag(110) layers at low coverages do not give rise to a LEED pattern intense enough to be easily recognized. If this is the case, the substrate (1×1) pattern will dominate. HEED is quite sensitive to small islands on a substrate as demonstrated by our present measurements. Apart from the above question, our results and the results of Lince *et al.* are mutually consistent. They also observed clustering of Ag upon annealing with the reappearance of Ge(100)-(2×1) and concluded that the Ag-Ge interaction was weak.

From our core-level intensity measurements (Fig. 4) and the Auger intensity measurements of Lince *et al.*, the Ge substrate must be fairly well covered by Ag for one monolayer coverage. Because of the uncertainties in our intensity measurements and the uncertainties in the electron-escape depth, we are not certain if three-dimensional growth already starts below monolayer coverage after nucleation. If three-dimensional growth proceeds right after nucleation, the growth mode is called the Volmer-Weber mode. If three-dimensional growth occurs only after the completion of the first monolayer the growth mode is called the Stranski-Krastanov mode. Because the nucleation starts at $\frac{1}{3}$ ML and the Ag film is quite flat for coverages up to about 2 ML (no detectable three-dimensional structure with HEED), there is perhaps very little practical difference between these two possibilities for the present case. A fraction of the Ge surface is probably still uncovered after three-dimensional growth starts elsewhere on the Ge surface. Some surface defects always exist, and they may affect the exact details of film growth. Growth of Ag at elevated temperature, on the other hand, is definitely described by the Volmer-Weber mode.

In a recent study of the Ag-Ge(111) interface prepared at room temperature, Rossi *et al.*[8] explain their results in terms of a model in which a strong chemical interaction took place at the interface resulting in a complex interface with a narrow intermixed region, two or three layers thick, and almost pure Ag islands grown on top of it. Since chemical reaction and atomic intermixing are not expected to be critically dependent upon crystal faces for real systems with defects, their model is at variance with ours. They based their conclusions on the following observations: (1) The Ag $3d$ intensity for submonolayer coverages was about 30% less than expected for smooth-layer formation from linear extrapolation of data at the lowest coverage of 0.08 ML. This was taken as evidence of Ag penetration into Ge. (2) The valence-band structure derived mainly from the Ge $4s$ states at about 10.5 eV below the Fermi level shifted toward lower binding energies with increasing Ag coverage. The shift was saturated at about 0.3 eV for Ag coverages greater than about 1 ML. This was taken as evidence of chemical interaction with a resultant reduced valence-band width. (3) The Ge $3d$ intensity after Ag coverage was more than expected for smooth-Ag-layer growth. This was taken as evidence of mixing and/or uneven growth.

Evidence described in (1) above is really too weak to be conclusive. If the error bars indicated by Rossi *et al.* (Fig. 5 of Ref. 8) are taken into account, one can easily show that their data are also consistent with a model in which no penetration of Ag into Ge occurs. Specifically, the dashed line in that figure can be redrawn to have a smaller slope and to pass through the origin and all error bars associated with data points for $\Theta < 1$ ML (the reduced intensity scale should be changed correspondingly).

Evidence described in (2) above is also too weak to be conclusive. The Ge $4s$ photoemission structure is very broad and asymmetric, so it is difficult to determine its position precisely. Furthermore, the shift may be due, at least in part, to changes in band bending occurring with the deposition of a metal. The band bending as a function of Ag coverage can be determined precisely by measuring the Ge core-level position if the interface chemical shift is very small [which is true for Ag-Ge(100)]. A core-level shift of about 0.2 eV towards lower binding energies was reported by Rossi *et al.* for Ge(111), and this value is comparable to the reported shift in the Ge valence $4s$ states of approximately 0.3 eV, also towards lower binding energies. So the net shift in the Ge $4s$ states is extremely small, if nonzero. Considering the experimental accuracy, the results are not conclusive.

Evidence described in (3) above is consistent with three-dimensional growth or the existence of pinholes or cracks in the overlayer, as we have shown that intermixing does not occur. By measuring the attenuation of the Auger signal from the Ge(111)-(2×8) substrate as a function of Ag coverage at room temperature, Berturcci *et al.*[15] concluded that Ag growth was layer-by-layer (Frank—van der Merwe mode) on Ge(111)-(2×8). Since the (2×8) reconstruction is suppressed by Ag coverage, it seems reasonable to assume that layer-by-layer growth of Ag also occurs on Ge(111)-(2×1) which is the reconstruction for samples obtained by cleavage at room temperature (this is the type of sample used by Rossi *et al.*). If this assumption is valid, then the evidence described in (3) above could be explained as due to pinholes or cracks in the Ag overlayer. Practically all samples prepared by cleavage have some defects or steps over an area of macroscopic scale, and these defects or steps could conceivably produce pinholes or cracks in the overlayer. We do not know if the above explanation applies to the data in Ref. 8, because no details about surface quality were given.

Therefore, our results and conclusions are not inconsistent with the data reported in Ref. 8, when experimental uncertainties are taken into account.

V. CONCLUSIONS

A detailed investigation of the Ag-Ge(100) interface using photoemission spectroscopy and HEED has been made. The major experimental results are summarized in the previous section. The crystallographic relationships, growth mechanism, chemical interactions, and electronic properties are discussed. The results provide a fairly clear picture of the interface behavior. Another purpose of the present research is to determine the Ge(100)-(2×1) surface structure by examining the spectroscopic and structural information as a function of Ag coverage. From our results, we can only say that the vacancy models are most likely not correct. More research is definitely needed. By using other adsorbates which interact differently with Ge(100)-(2×1) than Ag, it is hoped that in the future we will be able to distinguish different surface sites, if they exist (such as predicted by the asymmetric dimer model), through selective adsorption, so that a more definitive picture about the surface reconstruction of Ge can be obtained.[16]

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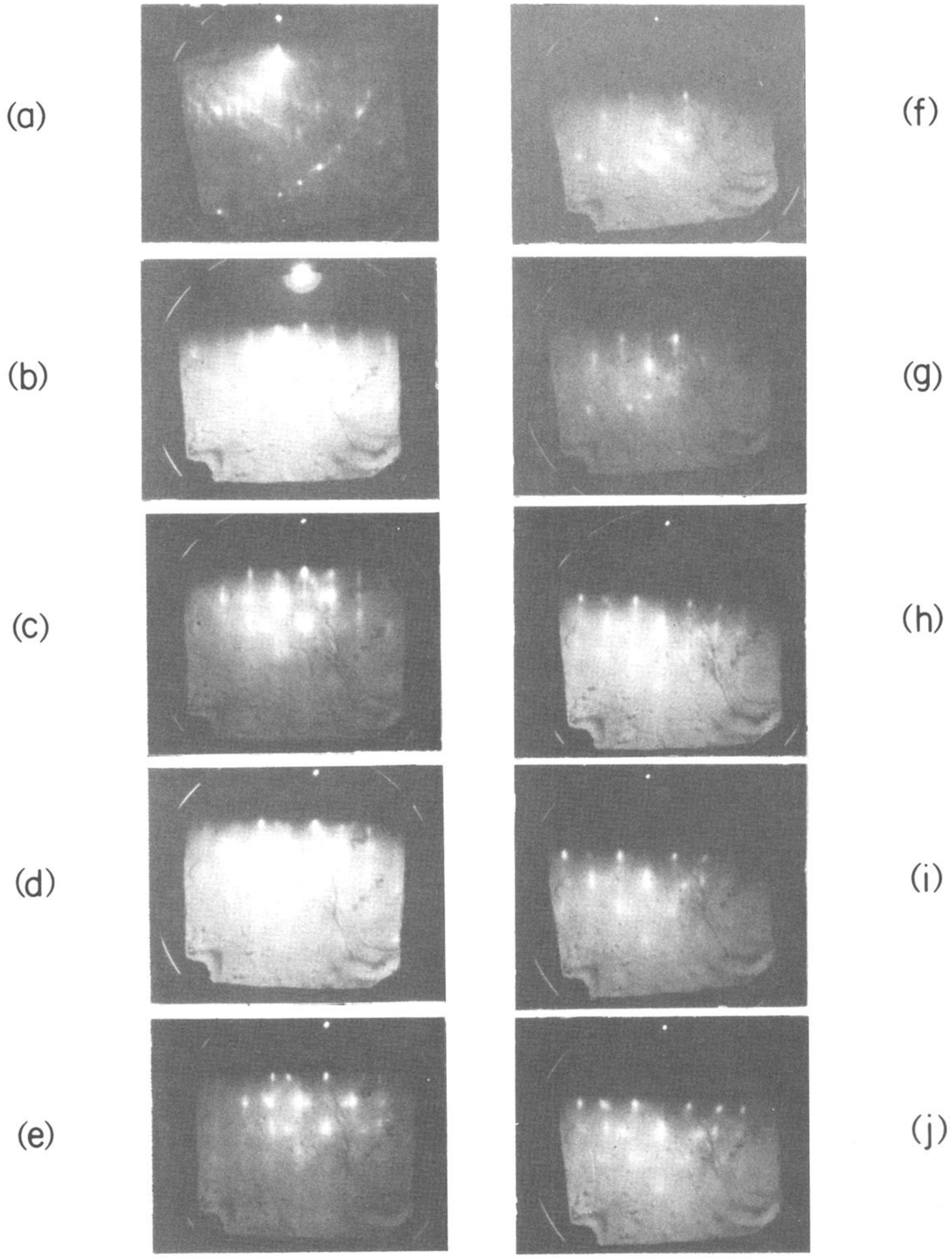

FIG. 1. HEED patterns for (a) clean Ge(100)-(2×1) and (b)—(j) the same surface covered with Ag. The patterns on the left and right are with the incident electron beam aligned approximately with the Ge[011] and Ge[0$\bar{1}$1] directions, respectively. The Ag coverages are as follows: (b) and (f) 2 Å; (g) 5 Å, (c) and (h) 10 Å; (d) and (i) 20 Å; (e) and (j) 40 Å. The electron-beam energy was 8 keV. Some pictures were overexposed in order to show some relatively faint diffraction streaks.