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Determination of the bonding and growth of Ag on Si(100)-(2$\times$1)

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The bonding and growth of Ag on Si(100) were studied with high-resolution photoemission spectroscopy and high-energy electron diffraction. By monitoring the changes in the Si 2*p* core-level and Ag 4*d* valence-band line shapes, we have examined the chemical interaction between the Ag adatoms and Si surface dimer atoms. The Ag-to-Si bonding coordination number as a function of coverage was obtained. This number is 2 at low Ag coverages, which suggests that the bonding site for a Ag adatom is between two neighboring Si surface dimers along the direction of dimerization; the two dimer dangling bonds pointing at the Ag adatom join the two Ag *sp* hybrid orbitals to form two Ag—Si bonds. The growth mode was observed to be three dimensional at higher coverages. The Schottky-barrier height was measured.

I. INTRODUCTION

The formation of metal-semiconductor interfaces has been a subject of considerable interest both scientifically and technologically. Specifically, there have been numerous studies of the noble-metal–elemental-semiconductor systems for a better understanding of the overlayer growth behavior and the resulting structure and properties.[1–10] Many of these systems show a three-dimensional growth behavior at high coverages. However, the complexities at the interfacial region can cause significant differences in behavior among these systems at the initial stages of growth. The interface structure, including the degree of intermixing, overlayer morphology, and epitaxial relationship, can also strongly depend on the growth conditions such as the sample temperature.

Previous photoemission studies of metal-semiconductor systems have generally focused on interfacial properties for thicker overlayers, the Schottky barrier, for example. Yet a detailed picture of the atomic bonding and interaction right at the interface is generally lacking, although it is clearly an important and fundamental step toward understanding the interface properties. This information can be obtained by using high-resolution photoemission spectroscopy as a local probe of the atomic environment during the initial stages of interface formation. This paper presents such a study of the Ag-Si(100) system prepared by depositing Ag onto Si(100)-(2$\times$1) at temperatures between 50 and 100 °C. The resulting system is characterized by an abrupt interface, thus considerably simplifying the analysis of the data. In contrast, the interfaces formed by depositing Au or Cu on Si or Ge generally show substantial intermixing.[1–10] The different behavior of the Ag-overlayer systems compared with the Cu- and Au-overlayer systems is an interesting phenomenon. Since the reactivity between Ag and Si is very low, it is expected that the interface characteristics at low Ag coverages as determined in this study remain unchanged for higher coverages.

The present study employs high-resolution core-level photoemission to obtain information about the selective modification of the atomic sites on the substrate surface,[11–14] from which the character of the bonding is deduced. The line shape of the Ag 4*d* states as a function of coverage is investigated, which gives a measure of the Ag-Ag interaction. The band bending induced by Ag adsorption and the Schottky-barrier height are determined by monitoring the bulk Si 2*p* core-level position as a function of the overlayer thickness.

II. EXPERIMENTAL DETAILS

The photoemission measurements were performed at the Synchrotron Radiation Center of the University of Wisconsin–Madison at Stoughton, Wisconsin. Light from the 1-GeV storage ring Aladdin was monochromatized by the "Extended Range Grasshopper" monochromator of the University of Illinois beam line. The photoemitted electrons were analyzed with a cylindrical-mirror analyzer. The Fermi edge of a polycrystalline gold foil in electrical contact with the sample was used as the energy reference. The width of the Fermi edge was measured as a function of photon energy, giving an overall resolution of about 0.2 eV for the experiment.

The photoemission chamber, having a typical base pressure of 10^{-10} torr, is equipped with a high-energy electron-diffraction (HEED) system, an Auger system, evaporators consisting of shutters and tungsten crucibles heated by an electron beam, and a quartz crystal thickness monitor for determining the deposition rate. The *n*-type Si(100) substrates were prepared from commercial wafers, and were etched in concentrated nitric acid before insertion into the vacuum chamber. The substrates were cleaned in the vacuum chamber by thermal annealing at about 1100 °C for 10 s or more.[13] The long-range order and flatness of the surface were checked by HEED, which showed a sharp two-domain (2$\times$1) pattern with a very slight mixture of (2$\times$2). Ultrapure Ag was evaporated at a rate of 0.5 monolayer (ML) per minute. 1 ML here is referred to as 6.8×10^{14} atoms/cm^2, the site density for the unreconstructed Si(100) surface. Prior to each Ag deposition and subsequent photoemission measurement, the Si(100) sample was cleaned and allowed to cool down to between 50 and 100 °C. The sample was examined with HEED again after the photoemission measurement.

III. RESULTS AND DISCUSSION

A. High-energy electron diffraction and growth mode

The three-dimensional growth behavior of Ag on Si(100) can be expected from the lower surface energy of Si compared to Ag.[15] This is indeed observed by HEED. As the coverage of Ag on Si(100) increases, the intensity of the $\frac{1}{2}$-order diffraction spots slowly decreases, and extra spots corresponding to Ag(111) gradually appear.[16] The $\frac{1}{2}$-order spots of Si(100) are still visible (although extremely weak) at a 10-ML coverage, indicating the island nature of the Ag growth. Some extra spots, less intense than the (111) spots, also appear in the HEED pattern for coverages of $\Theta > 4$ ML.[1,17] The three-dimensional growth behavior has also been confirmed in this experiment by observing the nonexponential decay of the Si $2p$ core-level photoemission intensity for increasing Ag coverages. Since Ag adsorption does not induce a reconstruction of a different periodicity, it cannot be decided from HEED alone whether the growth mode is of Stranski-Krastanov (formation of a uniform interface layer followed by three-dimensional growth) or of Vomer-Weber type (three-dimensional growth from the start).

B. Valence-band photoemission and Ag-Ag interaction

The valence bands of Si and Ag were measured with a photon energy of 55 eV, and some of the spectra are shown in Fig. 1, with the Ag coverages indicated. The clean Si(100) valence-band features comprise a peak at a binding energy of about 1 eV, derived from the Si(100) surface states, and three broad features at higher binding energies corresponding to features in the bulk valence density of states. The surface states have been investigated in detail previously by angle-resolved photoemission.[18-20] For the lowest Ag coverage of 0.05 ML, the Ag $4d$-derived band is visible as a small peak at about 6 eV with respect to the Fermi edge E_F, superimposed on the Si valence-band features. As the Ag coverage increases, the Si-derived features are attenuated in the spectra, while the Ag $4d$-band feature becomes more intense and broader. The broadening and the development of structures in the Ag $4d$ line shape are indicative of the interaction between the Ag atoms associated with island formation; the interaction results in the formation of Ag $4d$ valence bands.[8] The Ag $4d$ width, defined here as the full width at half maximum of the Ag $4d$ feature, is shown in Fig. 2 as a function of Ag coverage. At the lowest coverages the narrow width of this peak suggests that the Ag adatoms are dispersed on the surface and, consequently, the width is determined by the substrate crystal-field effect and perhaps, to a lesser degree, the hole-lifetime broadening.

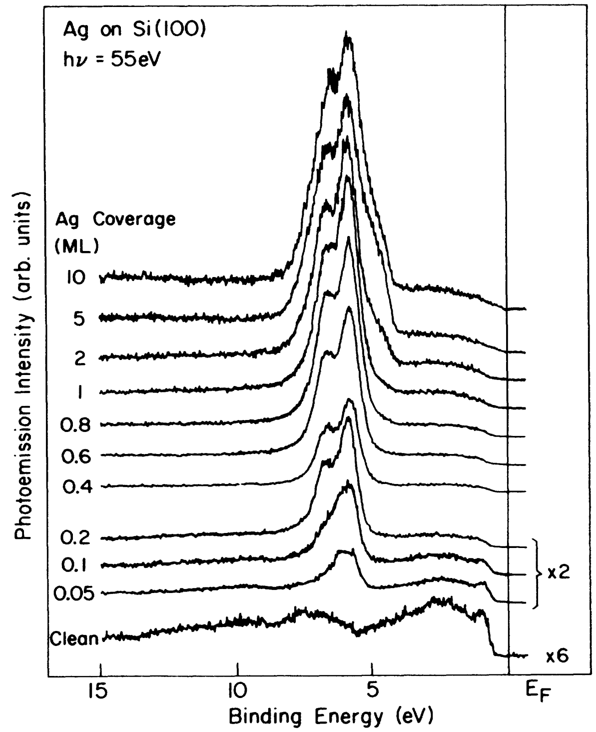

FIG. 1. Angle-integrated photoemission spectra for the valence-band region of Si(100) covered with Ag taken with a photon energy of 55 eV. The Ag coverages are indicated. The binding-energy scale is referred to the Fermi level at E_F.

C. Si 2p core-level photoemission

Some of the photoemission spectra of the Si $2p$ core level taken with a photon energy of $h\nu = 150$ eV are

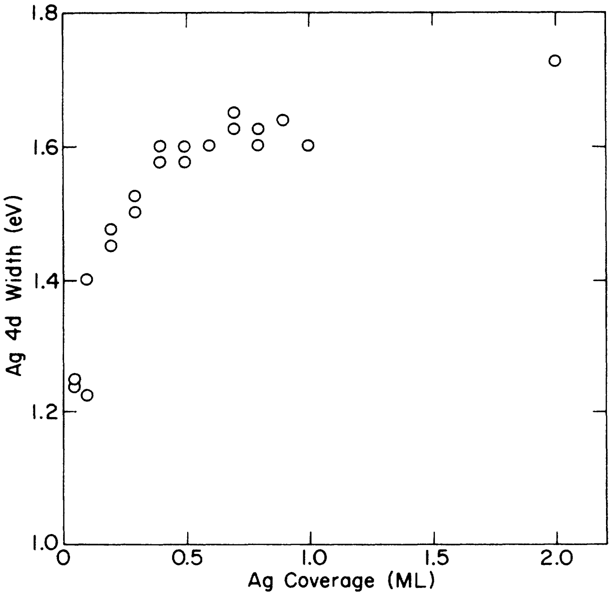

FIG. 2. Ag $4d$-band width (full width at half maximum) as a function of Ag coverage.

shown in Fig. 3; the Ag coverage is indicated for each spectrum. The photoelectron escape depth is on the order of 5 Å for this photon energy, resulting in a high surface sensitivity. Some additional spectra were also taken with $h\nu = 108$ eV (not shown here); these spectra mainly show the bulk contribution.[13,14,21] The relative binding-energy scale in Fig. 3 is simply the binding-energy scale (referred to the Fermi level) offset by a constant to bring the bulk Si $2p_{3/2}$ core level for the clean Si(100) surface to the origin. The core-level line shape for clean Si(100)-(2×1) has been investigated in detail previously using a least-squares-fitting procedure involving a model function which incorporates the essential physics of core-level photoemission; the analysis also includes a comparison of the bulk- and surface-sensitive spectra.[13,14,21] The result of the analysis shows that the spectrum consists of a bulk component and a surface-shifted component; the surface shift is 0.53 eV toward lower binding energies relative to the bulk component. Each component shows a spin-orbit splitting of 0.61 eV. The decomposition of the spectrum for clean Si(100)-(2×1) into the bulk (B) and surface (S) contributions and the overall fit to the data are indicated in Fig. 3 by the various curves. The details of the fitting procedure and the resulting data for the fit can be found in previous publications and will not be repeated here.[13,14,21–23]

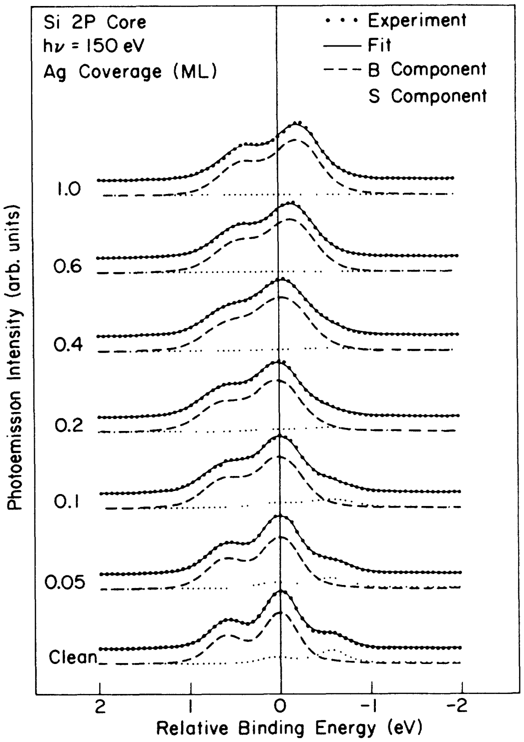

FIG. 3. Si $2p$ core-level spectra for clean and Ag-covered Si(100) taken with a photon energy of 150 eV. The results of a least-squares fit are indicated by the various curves for the overall fit and the bulk (B) and surface (S) contributions. The relative binding-energy scale is simply the binding-energy scale (referred to the Fermi level) offset by a constant to bring the bulk Si $2p_{3/2}$ core level for the clean Si(100) surface to the origin.

The surface atomic structure of Si(100)-(2×1) is known from recent scanning-tunneling-microscopy (STM) studies.[24] The (2×1) reconstruction is a result of the formation of dimers, which reduces the number of dangling bonds per surface Si atom from two for a (1×1) unreconstructed surface to one for a dimerized surface. The surface-induced core-level shift can be related to the difference in bonding environment for the surface dimer atoms (three-fold coordinated) relative to that for the bulk atoms (four-fold coordinated). The STM results also show that both buckled and nonbuckled dimers exist on a typical (2×1) surface with about equal population, and about 10% of the surface is covered by defects in the form of missing dimers. Previous photoemission studies have shown that the buckling does not lead to any appreciable core-level shifts, and the intensity of the surface-shifted core-level component seen in Fig. 3 corresponds to about 0.9 ML.[25] The departure from the ideal value of 1 ML has been attributed to the defects.

The same method of core-level line-shape analysis used for the clean surface was used to analyze the spectra for the Ag-covered surfaces; some of the results are shown in Fig. 3. Clearly, the main effect of increasing the Ag coverage is that the intensity of the surface-shifted Si $2p$ core-level component decreases relative to the bulk component. The simplest interpretation is that the Ag atoms form chemical bonds with the Si surface atoms, which then see a bulklike bonding environment and hence assume a bulklike core-level binding energy.[13,14] Therefore, in this picture a Si surface atom becomes fourfold coordinated after the Ag saturates its dangling bond. In fitting the spectra for Ag-covered Si(100), the Lorentzian width (lifetime broadening) of each spin-orbit-split component, the spin-orbit splitting, and the intensity branching ratio between the two spin-orbit-split components were assumed to be the same as those for the clean spectrum. However, the Gaussian width (instrumental, phonon, and inhomogeneous broadening) was allowed to vary. The Gaussian widths of the Ag-covered Si are about 10–20% greater than that of the clean surface, probably due to small unresolved shifts associated with the lack of long-range order and the random size distribution of the Ag islands at higher coverages.

D. Adsorbate–substrate bonding

From the results of the fit discussed above, we have computed the average number of Si surface dimer atoms converted to have a bulklike binding energy in the presence of each adsorbate Ag atom. Based on the above model, this number is just the Ag-to-Si bonding coordination number.[13,14] Figure 4 shows this number as a function of Ag coverage, which decreases from 2 at low coverages to about 1 at 1 ML coverage. At the lowest Ag coverages, the Ag adatoms are dispersed on the surface as discussed above. The simplest structural model for an isolated Ag adatom with a bonding coordination number of 2 is shown in Fig. 5. The model shows a Ag atom bonded between two neighboring Si surface dimers along the direction of dimerization; as a result of the bonding, the dangling bonds of the two Si atoms involved are saturated.

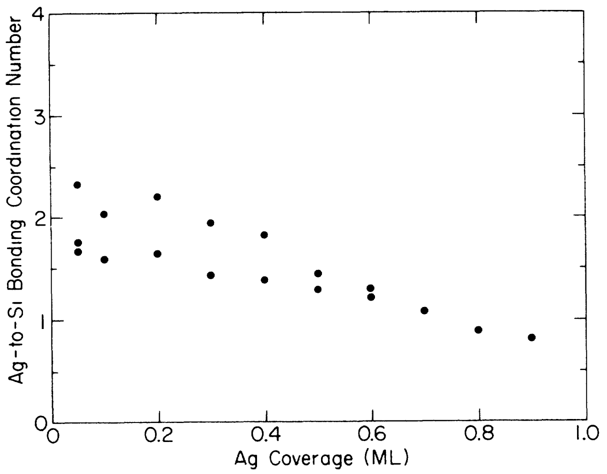

FIG. 4. Ag-to-Si bonding coordination number as a function of Ag coverage. This is the average number of Si atoms affected by each Ag adatom. For some coverages two or three data points are shown, corresponding to independent measurements starting from a fresh Si(100)-(2×1) substrate. The data scattering is due to limited experimental precision.

Ag, like Cu, is known to exist in several valence states including 1+, 2, and 3, although the 3+ state is extremely rare.[26–29] Examples of bicovalent Ag include $\mathrm{Ag[NH_3]_2}^+$ and $\mathrm{Ag[CN]_2}^-$, which have a linear geometry. In these compounds with a linear geometry, it is known from symmetry arguments that the bonding of Ag involves the *sp*-hybrid orbitals. In the present case of Ag on Si(100), the most favorable bonding configuration will undoubtedly depend on the structural constraints. The sum of the nominal covalent radii of Ag and Si is 2.7 Å, and the actual bonding distance cannot be very different from this value. Indeed, recent studies of Ag adsorbed on Si(111)-(7×7) with the technique of surface-extended x-ray-absorption fine structure yielded a Ag—Si bond length of about 2.5 Å,[2] although the distance for Ag on Si(100) is not necessarily the same and is not known. The distance between the two Si dimer atoms involved in the Ag—Si bonding (see Fig. 5) is about 5.3 Å according to the usual dimer model,[30] which is supported by the STM result.[24] Since this distance is about twice as large as the Ag—Si bond length, it is reasonable to assume that the Ag adatom falls right in between the two Si atoms. With this linear-bonding geometry, there will be little bond stretching and/or compression. However, the dangling bonds on the two surface Si atoms will be rotated from the most favorable orientations. Generally speaking, it is energetically easier to rotate bonds than to change the bond length substantially; thus, the actual geometry must be fairly close to the proposed linear configuration involving the usual *sp*-hybrid bonding of the Ag.

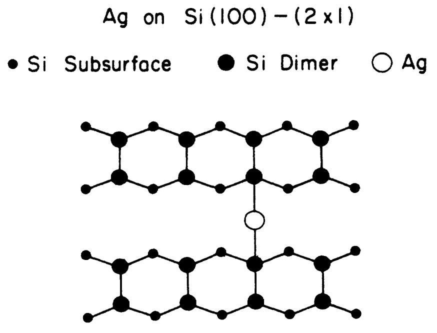

FIG. 5. Top view of a structural model for an isolated Ag adatom bonded onto Si(100)-(2×1).

When the Ag coverage increases, the "grooves" between the Si dimer rows become gradually filled with Ag according to the above model. In addition, some of the Ag adatoms will form clusters. The degree of Ag aggregation is indicated by the Ag 4*d*-band width (Figs. 1 and 2). Based on a consideration of the areal densities of the Si surface dimer bonds and the Ag atoms in a Ag(111) monolayer, it is evident that the average Ag-to-Si bond number will be less than 2 after Ag(111) islands form on the surface. This is consistent with the experimental finding shown in Fig. 4, namely the average bonding coordination number decreases as the coverage increases. The data in Fig. 4 do not show an abrupt transition at 0.5-ML coverage because the sample consists of Ag adatoms in the "grooves" as shown in Fig. 5 and Ag(111) islands (clusters). The detailed bonding between the Ag islands and the Si substrate cannot be determined based on the present data, but it quite likely involves the bonding of some of the Ag atoms with the Si dangling bonds, while the Ag atoms in an island are held together by metallic bonding. The Ag—Si bonds may not be as localized as for an isolated Ag adatom, as the metallic bonding within the Ag island may tend to spread out the bond charge.[31]

E. Comparison with Ag on Ge(100)-(2×1)

It is interesting to note that the growth behavior of a closely related system, Ag on Ge(100)-(2×1), is very similar. But the core-level shift induced by adsorption, reported in a previous study, is different.[8] The first monolayer of Ag on the Ge(100) surface does not cause any noticeable changes in the Ge 3*d* core-level line shape; thus the surface core-level binding energy is not affected by the Ag adsorption. To explain this different core-level shift, one needs to examine the nature of the bonds involved. The present results for Ag on Si implies that the Ag-Si bond is essentially covalent; thus the Si surface atoms after Ag adsorption "see" a bulklike bonding environment and therefore "assume" a bulklike core-level binding energy. Indeed, the electronegativities of Ag and Si are fairly close;[32] thus, one expects the bonding to be nearly covalent. Ge, on the other hand, is known to have a significantly larger electronegativity than Si. Therefore, the Ag—Ge bond would be partially ionic, with the Ge being negatively charged. This would then raise the average electrostatic potential energy of a core electron centered about the Ge nucleus, leading to a binding-energy shift to a smaller value. The surface core-level binding energy of clean Ge(100)-(2×1) is 0.43 eV smaller than the bulk value. After Ag adsorption, the surface shift would be suppressed if Ge had the same electronegativity as Ag. However, the partially ionic nature of the bond causes a chemical shift for the surface Ge atoms toward lower binding energies. This explains the direction of the shift. In several other related systems [In, Sb, As, Sn, S, O, Cl, and F adsorbed on Ge(100) and/or Si(100)] the experimentally observed direction and magnitude of the adsorbate-induced chemical shifts show a good correlation with the electronegativity differences.[11,13,14,33–38] By linear interpolation based on these results, the estimated Ag-induced chemical shift for Ag on Ge is indeed very close to the original surface shift. Thus, the seemingly insensitivity of the Ge-surface core-level position to Ag adsorption is a result of the fortuitous near equivalence of the clean surface shift and the Ag-induced chemical shift.

F. Schottky barrier

At the metal-semiconductor interface, the discontinuity in the electronic properties results in the formation of a Schottky barrier.[5] The alignment of the Fermi level across the interface causes the valence bands of the semiconductor to bend near the interface. This effect can be observed in the photoemission spectra of the Si $2p$ core level. In Fig. 4 the bulk contribution of the Si $2p$ core level shifts towards lower binding energies for increasing Ag coverages (the surface-to-bulk shift remains unchanged). Since the binding-energy scale in Fig. 4 is directly tied to the Fermi level, this shift is a result of the band bending occurring near the surface. From the measured shift we have deduced the position of the Fermi level relative to the Si valence-band maximum (VBM);[11,14] the result is shown in Fig. 6. For the clean surface the Fermi level is at 0.41 eV above the VBM. The band bending appears to be saturated for coverages more than 1 ML; the final Fermi-level position is at 0.23 eV above the VBM. For our *n*-type Si substrate this result gives a final Schottky-barrier height of about 0.9 eV.

IV. SUMMARY AND CONCLUSIONS

Using photoemission and high-energy electron-diffraction techniques we have examined the growth behavior and the resulting structure and properties of Ag on Si(100)-(2×1). For deposition at temperatures between 50 and 100 °C, the system was found to grow in a three-dimensional manner. At low coverages the Ag adatoms are dispersed, and each Ag adatom saturates two Si surface dangling bonds. The result implies a bonding site in between two neighboring Si surface dimers, and the bonding for the Ag adatom involves the two sp-hybrid orbitals, resulting in a (nearly) linear bonding geometry. The result is compared with that for Ag deposited on Ge(100) under similar conditions. The differences are explained in terms of the differences in electronegativities. The energy position of the Fermi level with respect to the Si VBM for regions near the interface was measured as a function of Ag coverage, and the Schottky-barrier height was determined.

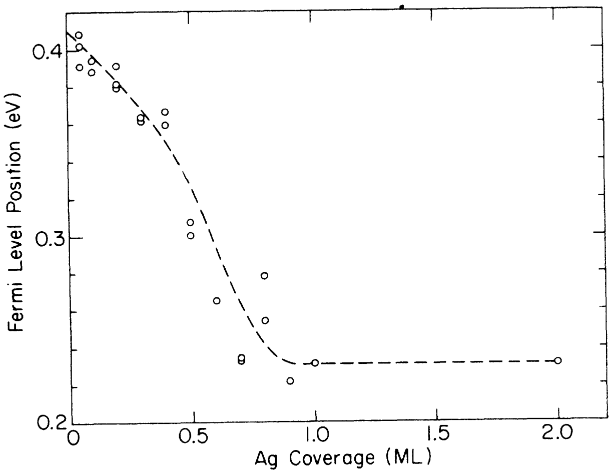

FIG. 6. Fermi-level position relative to the valence-band maximum as a function of Ag coverage. The dashed curve is just a guide to the eye. The conduction-band minimum is at 1.12 eV at 300 K.

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