Observation and Origin of Extraordinary Atomic Mobility at Metal-Semiconductor Interfaces at Low Temperatures

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Extraordinarily high mobility of Si and Ge atoms at semiconductor (Si, Ge)-metal (Al) interfaces is observed at temperatures as low as 80 K during thin metal film deposition. *In situ* x-ray photoemission spectroscopic valence-band measurements reveal a changed chemical bonding nature of the semiconductor atoms, from localized covalentlike to delocalized metalliclike, at the interface with the Al metal. The resulting delocalized bonding nature of the interfacial semiconductor atoms brings about the observed extreme enhancement of their mobility. The finding opens avenues for tailoring reaction kinetics and phase transformations in nanostructured materials, as functional thin-film systems, at ultralow temperatures by dedicated interfacial design.

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Atomic mobility in solid materials controls the occurrence and rate of many important material processes, such as (inter)diffusion, chemical reactions, phase transformations, crystal nucleation and growth, as well as recovery and recrystallization [1,2]. In general, energy barriers exist for the movement of atoms in a solid and, consequently, the movement of atoms in a solid is usually thermally activated. Accordingly, atomic mobility is strongly dependent on the temperature, in addition to the structure and the bonding nature (covalent, metallic, or ionic) of the material [3]. The atomic mobility can be enhanced at the surface and interface of materials, due to specific structural, chemical and/or electronic modifications at these locations [4–8]. Evidently, a fundamental understanding and (local) command of atomic mobility are crucial for tailoring the reactivity and long-term stability of materials and their assemblies during processing and service.

In this work, extreme enhancement of the mobility of Si and Ge atoms at amorphous semiconductor- (Si, Ge)-metal (Al) interfaces was detected at temperatures as low as 80 K. A 1-nm amorphous Ge (a-Ge) layer was observed to be "floating" continuously on top of an epitaxially growing Al layer at 80 K, indicating pronounced atomic mobility of Ge atoms at the Ge/Al interface at such an ultralow temperature (i.e., at $T = 0.066T_m^{\mathrm{Ge}}$, where T_m is the melting point). Similar behavior was observed for a 1-nm amorphous Si (a-Si) layer on top of Al at 80 K. *In situ* x-ray photoemission spectroscopy (XPS) valence-band measurements unambiguously demonstrated the occurrence of the modified chemical bonding nature of the semiconductor atoms at the interface with Al, which provides the basis for the observed extreme enhancement of the atomic mobility at the semiconductor–metal interfaces. Such high atomic mobility at ultralow temperatures ($T < 0.1T_m$), occurring exclusively at interfaces, may be exploited to enable and/or enhance the phase-transformation and reaction kinetics in nanostructured materials and thin-film systems at low temperatures, as, for example, desired in the manufacturing and low-temperature processing of heat-sensitive materials and their assemblies for various state-of-the-art technologies [9–13].

The experiments were carried out in an ultrahigh-vacuum (UHV) system ($<2 \times 10^{-10}$ mbar). A 50-nm single-crystalline Al(111) film with an atomically flat surface was prepared on a Si(111) substrate by thermal evaporation deposition followed by postdeposition annealing at 300 °C for 1 h in UHV. The specimen was then cooled to 80 K in UHV on a cooling stage with liquid-nitrogen flow. Next a 1-nm amorphous Si or Ge layer was deposited onto the cooled Al(111) surface by thermal evaporation. Finally, a 20-nm Al overlayer was deposited by thermal evaporation (deposition rate 10 nm/ min), again at 80 K. The thus-prepared specimens, referred to as $\mathrm{Al}_{20\text{-nm}}|\mathrm{Si}_{1\text{-nm}}|\mathrm{Al}(111)$ and $\mathrm{Al}_{20\text{-nm}}|\mathrm{Ge}_{1\text{-nm}}|\mathrm{Al}(111)$, respectively, were removed from UHV for subsequent investigation by Auger electron spectroscopy (AES) depth profiling and by cross-sectional TEM. See the Supplemental Material [14] for more experimental details.

The AES composition (elemental)-depth profile of the $\mathrm{Al}_{20\text{-nm}}|\mathrm{Si}_{1\text{-nm}}|\mathrm{Al}(111)$ specimen is shown in Fig. 1(a). The remaining part (see following) of the original a-Si layer is clearly resolved at the depth (of deposition) of about 20 nm below the surface. However, unexpectedly, a significant amount of Si is also found at the outer surface of the specimen (i.e., on top of the 20-nm thick Al top layer). Note that no Si could be detected within the 20-nm Al

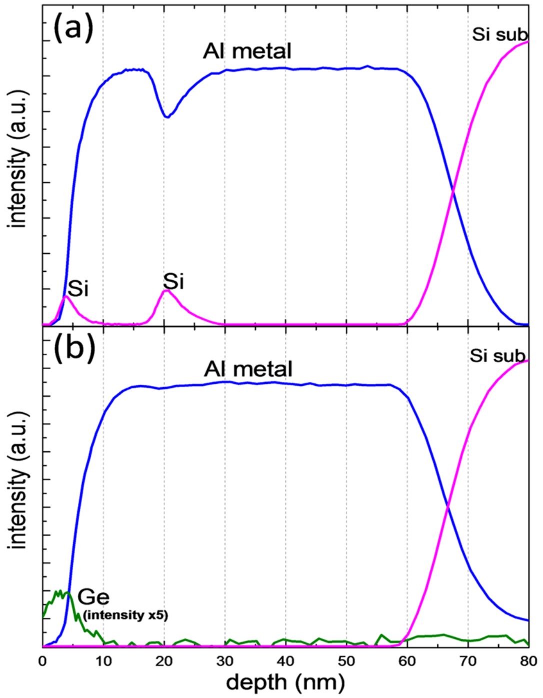

FIG. 1 (color online). AES composition (elemental)-depth profiles of the (a) $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Si}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ and (b) $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Ge}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimens.

overlayer by AES. The AES composition (elemental)-depth profile of the $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Ge}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimen is shown in Fig. 1(b). Very strikingly, no Ge is detected at the depth (of deposition) of about 20 nm below the surface; instead, the entire 1-nm thick Ge layer has relocated on top of the subsequently deposited Al layer.

Detailed, atomic-scale analyses of the cross section of the $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Si}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimen by energy-dispersive x-ray spectroscopy (EDX) elemental mapping and HRTEM are shown in Fig. 2. An EDX line scan of the Si-K signal from the top surface to the Al(111) substrate revealed the (exclusive) presence of Si both at its original (sandwiched) location and at the outer surface [Fig. 2(a)], which is fully consistent with the AES analysis [Fig. 1(a)]. Corresponding EDX mappings of the Si-K and Al-K signals of the specimen are shown in Figs. 2(b) and 2(c), respectively. The Si-K mapping clearly evidences the partitioning of the original 1-nm Si layer into two laterally more-or-less homogenous sublayers present at just below and above the subsequently deposited Al layer [Fig. 2(b)]. The corresponding cross-sectional HRTEM image of the specimen is shown in Fig. 2(d). This HRTEM image demonstrates that the Al overlayer had grown epitaxially with respect to the Al(111) substrate [see the fast Fourier transform (FFT) of the HRTEM image in the inset of Fig. 2(d)]. No lattice fringes corresponding to crystalline Si can be detected in the HRTEM image, indicating an amorphous state of the Si phase below and above the epitaxially grown Al layer (see above).

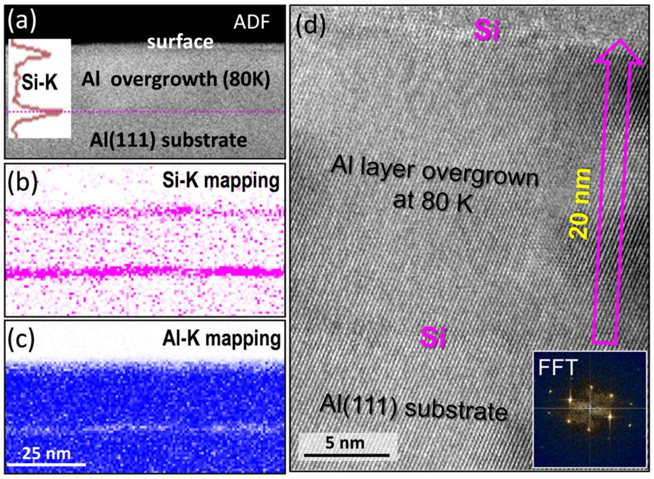

FIG. 2 (color online). Cross-sectional EDX and HRTEM investigation of the $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Si}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimen. (a) Annular dark-field (ADF) TEM image. An EDX line scan of the Si-K signal from the top surface to the Al(111) substrate has been incorporated in the image. (b),(c) EDX mappings of the Si-K and Al-K signals, respectively, of the same location as in (a). (d) Cross-sectional HRTEM image, with its FFT shown in the inset.

Cross-sectional EDX mapping and HRTEM analyses of the $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Ge}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimen are shown in Fig. 3. In agreement with the measured AES composition-depth profile [Fig. 1(b)], practically the entire 1-nm Ge layer has relocated at the outer surface (i.e., on top of the subsequently deposited Al layer). Only a tiny trace of Ge can be detected at the original (sandwiched) location, about 20 nm below the outer surface: see the EDX line scan of the Ge-K signal in Fig. 3(a) and the EDX mappings of the

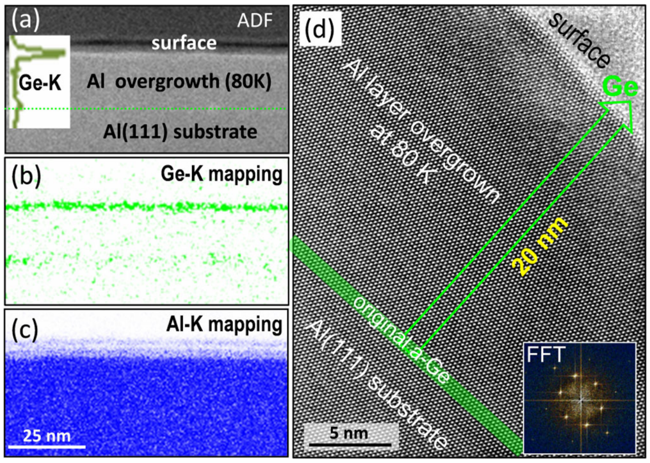

FIG. 3 (color online). Cross-sectional EDX and HRTEM investigation of $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Ge}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimen. (a) ADF TEM image. An EDX line scan of the Ge-K signal from the top surface to the Al(111) substrate has been incorporated in the image. (b),(c) EDX mappings of the Ge-K and Al-K signals, respectively, of the same location as in (a). (d) Cross-sectional HRTEM image, with its FFT shown in the inset.

Ge-K and Al-K signals in Figs. 3(b) and 3(c), respectively. The corresponding cross-sectional HRTEM investigation [Fig. 3(d)] revealed the occurrence of an epitaxially grown Al overlayer without indication of any (Ge) inclusion in the overgrown layer. These observations strongly indicate that the original 1-nm Ge layer has repositioned itself continuously to the top surface during the subsequent Al deposition step at 80 K. Such a floating Ge film layer appears to be continuous [see Figs. 3(a) and 3(b) and the corresponding high angle annular dark-field-STEM images shown in the Supplemental Material [14]], and no particles of crystalline or amorphous Ge could be indicated.

Therefore, both AES and cross-sectional TEM investigations have evidenced the striking relocalization of the Si layer in the $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Si}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimen, and more pronouncedly, the relocalization of the Ge layer in the $\mathrm{Al}_{20-\mathrm{nm}}|\mathrm{Ge}_{1-\mathrm{nm}}|\mathrm{Al}(111)$ specimen, during Al layer deposition even at 80 K. Obviously, in order to realize such continuous relocalization of the Ge (Si) layer, Ge (Si) and/or Al atoms must be able to diffuse in the thin Ge (Si) layer during Al deposition. Considering the similar sizes of Al and Ge (Si) atoms [15], the possible diffusion of Al in the Ge (Si) layer should be realized by a substitutional-type (rather than an interstitial-type) diffusion mechanism, which requires a high mobility of Ge (Si) atoms in the layer. Therefore, irrespective of the exact operating diffusant [Ge (Si) or Al, or both], the above experimental observations indicate compellingly the occurrence of an anomalously high Ge (Si) atomic mobility in the semiconductor Ge (Si) layer in contact with the Al metal at very low temperatures.

The atomic mobilities of Si and Ge at low temperatures in bulk Si and bulk Ge are extremely small, owing to the strong covalent bonding of the semiconductor atoms [3] (bond energies of 2.34 eV for Si–Si and 1.95 eV for Ge–Ge [16]). At room temperature, any (inter)diffusion of Si and Ge is practically impossible (self-diffusion lengths for 120 s at RT, extrapolated from diffusion data at high temperatures, are 1.9×10^{-27} m in Ge bulk [17] and 2.5×10^{-41} m in Si bulk [18]). Against this background, the very high mobility of Si and Ge atoms at the a-Si/Al and a-Ge/Al interfaces at 80 K ($T < 0.1 T_\mathrm{m}$) is very surprising.

To reveal the underlying mechanism for the strikingly high mobility at the semiconductor-metal interface, the electronic structure of interfacial Ge in contact with Al metal was investigated through *in situ* XPS valence-band (VB) measurements. Ultrathin Ge films [19] of different average thicknesses from 100 monolayers (MLs) (1 ML is defined here as the atomic diameter of Ge = 0.25 nm [15], corresponding to 1.1×10^{19} Ge atoms per unit film area) down to 1 ML were grown onto a clean Al(111) surface, which was cooled by liquid nitrogen. VB spectra were directly recorded *in situ* after deposition of the ultrathin Ge film of each thickness. The VB spectra of the ultrathin Ge films, resolved by subtracting the Al-substrate contribution from the measured spectra [20], are shown in Fig. 4(a) for various film thicknesses.

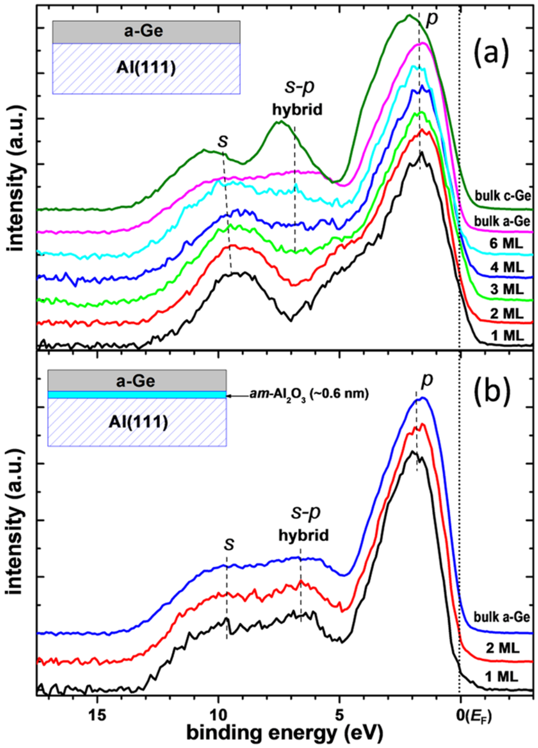

FIG. 4 (color online). (a) Evolution of the valence-band spectra (with E_F at 0 eV) of ultrathin Ge films on Al(111) with decreasing Ge thickness from *in situ* XPS measurements. The valence-band spectra of bulk a-Ge (100 ML) and bulk single-crystalline Ge (c-Ge) are shown for comparison. All the spectra have been normalized with respect to their maximum height and a constant offset in intensity has been added in order to avoid any overlapping of the spectra. (b) Measured valence-band spectra of 1-ML and 2-ML Ge thin films grown on 0.6-nm amorphous-$\mathrm{Al_2O_3}$/Al(111).

As follows from Fig. 4(a), for Ge film thicknesses ≥ 6 ML, the VB structure is comparable to that of bulk a-Ge (and also to that of small Ge clusters); i.e., a considerable intensity appears in the binding energy range of 6–7 eV, which is characteristic of a strong hybridization (sp^3) of s and p states occurring in the semiconductor Ge (or Si) bulk [21] or small clusters [22–24]. However, with decreasing Ge film thickness<6 ML, the s and p states in the Ge valence-band spectrum become gradually separated, resulting in a gradual disappearance of this s-p hybridization feature; the s-p hybridization feature has practically completely vanished for Ge film thicknesses of 2 ML and less. Such a nearly complete separation of s and p valence states has been predicted theoretically and observed experimentally for liquid Ge [25] in which any covalent bonding of Ge atoms by sp^3 hybridization has broken down and metallic bonding prevails instead [25–27]. Hence, the XPS VB study suggests that the chemical bonding of the interfacial Ge atoms in the very vicinity of metallic Al becomes similar to that in liquid Ge, which is metallic. A clearly observable increased number of electronic states at the Fermi level E_F for the ultrathin Ge films on Al (see the VB spectra of ultrathin Ge films in Fig. 4(a), and compare it with that of bulk *a*-Ge) is furthermore indicative of the metallic nature of *a*-Ge at the *a*-Ge/Al interface. This change of bonding character from (localized) covalentlike to (nonlocalized) metalliclike, in possible association with a high local density of vacancylike defects at the interface [8,28,29], is thereby the key for the surprisingly high mobility at the interface with Al even at 80 K. The atomic mobility (diffusivity) of metallized Ge can be estimated on the basis of the extrapolated self-diffusion data [30] in liquid Ge. This estimated diffusion coefficient of metallized Ge is in the range of 10^{-18}–10^{-17} $\mathrm{m^2\,s^{-1}}$ at 80 K, which results in a corresponding diffusion length (for 120 s) of about 10–30 nm, which is consistent with the observed length scale of mass transport pertaining to the experimental results. Recognizing the structural similarity of Si and Ge, a similar mechanism should also operate for Si (and presumably for other covalent semiconductors) in contact with Al, as already suggested by the here-observed very high mobility of Si at the interface with Al.

As follows from Fig. 4(a), the *s*-*p* hybridization feature emerges in the VB spectrum for *a*-Ge film thicknesses > 2 ML, implying that the Ge changes its bonding nature only in the very vicinity (i.e., at a distance ≤ 2 ML) of the Al metal. To substantiate the above experimental findings and interpretation, in a further experiment the clean Al(111) surface was first oxidized *in situ* (in 10^{-6} mbar of pure oxygen for 100 min) to form an atomically flat, 0.6-nm-thick amorphous-$\mathrm{Al_2O_3}$ insulator film at the surface [31,32], on which subsequently Ge films, with average thicknesses of 1 and 2 ML, were deposited under identical conditions as indicated above. The resolved (i.e., after subtraction of the substrate contribution) VB spectra of these 1- and 2-ML Ge films are shown in Fig. 4(b). Evidently, the ultrathin Ge films grown on the (0.6-nm) oxidized Al(111) substrate show a VB structure, which is practically identical to that of bulk *a*-Ge, which contrasts with the observations for ultrathin Ge films in direct contact with Al(111). These experiments convincingly show that Ge (and presumably other covalent semiconductors), only when in the very vicinity (distance ≤ 2 ML) of a metal, can change their covalent bonding nature to metallic nature and thereby gain an extraordinarily high interfacial mobility locally, at the interface with the metal, at low temperatures.

The modification of the electronic structure of a crystalline semiconductor by the presence of a nearby interface with a metal has been investigated by theoretical calculations, recognizing that under such a condition the electrons in the semiconductor would experience an additional image potential from the metal (i.e., a short-range electrostatic interaction occurs for electrons in the semiconductor and their image charges in the metal) [33–36]. These theoretical calculations have predicted that the band gap of the semiconductor can be significantly reduced or even closed in the very vicinity (≤ 5 Å [35], ≤ 10 Å [36]) of the metal, as a result of an image potential-induced local energy-band bending of the semiconductor. Consequently, the interfacial semiconductor may indeed become metallic. The theoretical prediction, together with recent experimental confirmations using ultrathin-film systems (see, e.g., Ref. [37]), agrees very well with the present experimental observations for ultrathin Ge films on the Al metal. However, these theoretical calculations on band-gap modification provide no direct information on the change of the nature of the chemical bonding in the semiconductor close to the interface with the metal. The present experimental XPS investigations have shown that the chemical bonding of amorphous Ge can become similar to that in liquid Ge and metalliclike close to the interface with a metal. The authors are not aware of any reported theoretical calculations for semiconductor-metal interfaces that predict such a modification of the chemical bonding nature of the semiconductor interface layer.

Deposition of Al onto the 1-nm thick *a*-Ge layer deposited on the Al(111) substrate, as performed in the present study, results in a doubling of the metalliclike interfacial Ge layer thickness (i.e., $2 \times 2\ \mathrm{ML} \approx 1$ nm), since the bonding-modification effect acts at the two opposite Ge/Al interfaces of the sandwiched Ge film. This suggests that practically all Ge atoms constituting the sandwiched 1-nm Ge layer gain an extreme atomic mobility and can all thus reposition themselves at positions such that the system Gibbs energy becomes reduced. There is practically no mutual solubility between Ge and Al at low temperatures (say, below 500 K) [38]. Then, considering the much smaller surface energy of *a*-Ge ($\gamma_{\{\mathrm{Ge}\}} = 0.7\ \mathrm{J\,m^{-2}}$ at 80 K [10]) as compared to that of Al(111) ($\gamma_{\langle \mathrm{Al}\rangle} = 1.1\ \mathrm{J\,m^{-2}}$ at 80 K [10]), the highly mobile Ge atoms will tend to move towards the top surface and the Al atoms will tend to diffuse towards the Al(111) substrate during Al deposition. As a consequence, the continuously deposited (and continuously with Ge "exchanged") Al can thus grow epitaxially on the Al(111) substrate (which is for this Al the thermodynamically most favored configuration), as observed. Such continuous atomic rearrangement in the evolving thin-film or substrate system, as driven by the lowering of the surface energy, is possible only due to the anomalously high mobility of the interfacial Ge atoms at the *a*-Ge/Al interface. Such surface-energy-driven movement can analogously occur for the Al/Si/Al(111) system, but in a possibly less outspoken way, as in this case the driving force is also positive but smaller ($\gamma_{\{\mathrm{Si}\}} = 1.0\ \mathrm{J\,m^{-2}} < \gamma_{\langle \mathrm{Al}\rangle} = 1.1\ \mathrm{J\,m^{-2}}$ [10,39]), which explains for this case the observed partitioning (i.e., only partial relocation) of the original 1-nm *a*-Si layer into two layers: one below and one above the overgrown Al layer.

Following the above discussion, it can further be predicted that the extraordinary atomic mobility would become less pronounced or even disappear if the Ge or Si layer on the metal becomes sufficiently thick or if it is instead deposited on an insulator surface. Corresponding, additional experiments, as also carried out in the present project, have indeed shown much reduced (Si, Ge) floating behavior for specimens including a thicker Ge layer or an ultrathin Al_2O_3 insulator layer (see the Supplemental Material [14]).

This work provides compelling experimental evidence for the occurrence of extraordinarily high mobility of interfacial Si and Ge atoms in contact with Al metal at temperatures as low as 80 K. A dedicated *in situ* valence-band XPS study unequivocally revealed a change of the bonding nature of an ultrathin Ge layer at the *a*-Ge/Al interface from localized covalentlike to delocalized metalliclike, which accounts for the observed extraordinarily high interfacial atomic mobility. These fundamental findings illuminate the possibly anomalous behavior of atoms at interfaces and thus provide avenues for tailoring reaction kinetics and phase transformations in nanostructured materials, as functional thin-film systems, at ultralow temperatures by dedicated interfacial design.

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[20] Except for the VB measurement of the clean Al(111) surface, the measured VB spectra constitute contributions from both the infinitely thick Al substrate and the ultrathin Ge film. To determine the VB spectra of the ultrathin Ge films of various thicknesses, the contribution from the Al substrate was subtracted from the measured VB spectra of the Ge-film–Al-substrate system, following the evaluation procedures developed by P. C. Snijders, L. P. H. Jeurgens, and W. G. Sloof in Surf. Sci. **496**, 97 (2002).
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