

## Band splitting of quantum wells of thin Ag films on Sn/Si(111) $\sqrt{3} \times \sqrt{3}$

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High-resolution valence band spectra of ultrathin Ag films on Sn/Si(111) $\sqrt{3} \times \sqrt{3}$  show intrinsic splitting of the quantum-well states (QWSs). Especially at low coverages, the QWSs of such a system display delicate coupling characters with the bulk bands from the substrate. The observed QWS splitting agrees well with the result of the theoretical calculation. We found that the splitting originates from an interface with a finite thickness. In addition, the interface also causes a large *sp* band splitting due to the Umklapp scattering in the  $\bar{\Gamma}$ - $\bar{M}$  direction of the Ag(111) surface Brillouin zone.

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Thin metal films on semiconductors are of fundamental scientific interest. Its structure facilitates an integration of physical and chemical properties of metal films with semiconductors, for example, magnetic coupling and oscillatory surface adsorption [1–4]. Thus, systematic studies of films with varying thicknesses in such systems might enable advanced material engineering, i.e., interfacial coupling and quantum interference [2]. Still, compared to studies that have been devoted to metal films on metal substrates, much fewer studies have been reported on semiconductor substrates. This is partly caused by the difficulty of growing epitaxial metal films on a semiconductor substrate due to the lattice mismatch. However, over the decades, significant efforts have been put into growing metal thin films on clean Ge or Si surfaces at reduced sample temperature [4–7]. Furthermore, recent progress in perfection of film preparation has made it possible to create atomically uniform films, facilitating highly precise measurements of the electronic structure including the interfacial structure [8–13].

The discrete quantum-well states (QWSs), due to spatial confinement of electrons in thin metal films, have been subjected to extensive studies. A simple, yet successful theoretical approach is to treat the electrons in the metal film as quasiparticles using the Bohr-Sommerfeld quantization rule. In this model the coupling of the QWSs with the electronic structure of the substrate is, however, entirely decoupled, i.e., only treating the electronic coupling as a boundary effect, which is represented just by a phase shift in the formula as an effective reflectivity. As demonstrated in the case of Ag films on Ge(111), the single-particle picture fails dramatically near a substrate band edge [8]. The unusual line shapes of the observed splits are shown due to many-body interactions and can be quantitatively explained by a Greens function calculation [9]. In addition, a peculiar bifurcation of the QWS bands was found to be related with the underlying interface when growing Ag films on Si(111) $7 \times 7$  [14].

In this study, valence electrons in the Ag films with energy and momentum inside the gap of the Si bulk bands can form fully confined QWSs. They disperse with in-plane momentum  $k_{\parallel}$ , shown as QWS bands. These bands may disperse inside the central zone of the Si bands, resulting in so-called partially confined resonance states. The Sn/Si(111) $\sqrt{3} \times \sqrt{3}$  surface

adapts a simple  $T_4$  model with 1/3 monolayer (ML) Sn and forms a nice flat surface with a minimum strain in contrast to the clean  $7 \times 7$  surface [14,15]. In this experiment, angle-resolved photoelectron spectroscopy was employed to map the dispersion of the QWS band along the main symmetry lines of the surface Brillouin zone (SBZ). At low coverages, the QWS bands follow the dispersions of the Si bands and form a zone area. The unusual band coupling precludes a single-particle explanation. As evidenced by DFT calculations, the coupling effect near a zone edge must be treated at the wave-function level, involving both the film and the substrate. Furthermore, our results show that each parabolic band splits into two subbands outside the zone of the Si band edges, which originates from an interface with a finite thickness.

Experiments were performed at beamline I4 at the MAX-lab synchrotron radiation facility in Lund, Sweden. Photoemission data were obtained with energy and angular resolutions of  $\sim 50$  meV and  $\pm 0.3^\circ$ . A hemispherical electron analyzer with a 2D detector (SPECS Phoibos 100) was used to measure the electronic band structure with the binding energy and the emission angle as two independent variables. The sample was rotated relative to the analyzer in steps of  $10^\circ$  to create a set of overlapping images, which were combined to create a wider angular span. The Si(111) samples (*n*-type, Sb-doped) with a resistivity in the range 1–10  $\Omega$ cm were preoxidized and cleaned *in situ* to create a  $7 \times 7$  surface. Evaporation of 0.4 ML of Sn followed by annealing at 620  $^\circ$ C for 2 min resulted in a sharp  $\sqrt{3} \times \sqrt{3}$  LEED (low-energy electron diffraction) pattern. Ag from a Knudsen cell were deposited on Sn/Si(111) $\sqrt{3} \times \sqrt{3}$  at 100 K. The surface was annealed at 300 K after deposition and then cooled back to 100 K for the measurement. The Ag evaporation rate was established using a quartz crystal thickness monitor and recalibrated against a formation of a Ag/Si(111) $\sqrt{3} \times \sqrt{3}$  surface [formed at  $\sim 0.56$  ML Ag based on atomic density of the Ag(111) surface] [16]. We denote film coverages following the conventional way, though noninteger coverage may exist at the interface.

Figure 1(a) shows a valence band image recorded with a photon energy of 21.2 eV from a 4-ML Ag film along the  $\bar{\Gamma}$ - $\bar{M}$  line of the Ag(111) SBZ. There is a strong emission of a surface state, just located at the  $\bar{\Gamma}$  point close to the Fermi level. As illustrated in Fig. 1(a), the valence bands of the Ag film clearly show dispersions of its quantum-well states. A paraboliclike metallic band ( $n = 1$ ) starts from  $k_{\parallel} = \pm 0.6 \text{ \AA}^{-1}$  at the Fermi-

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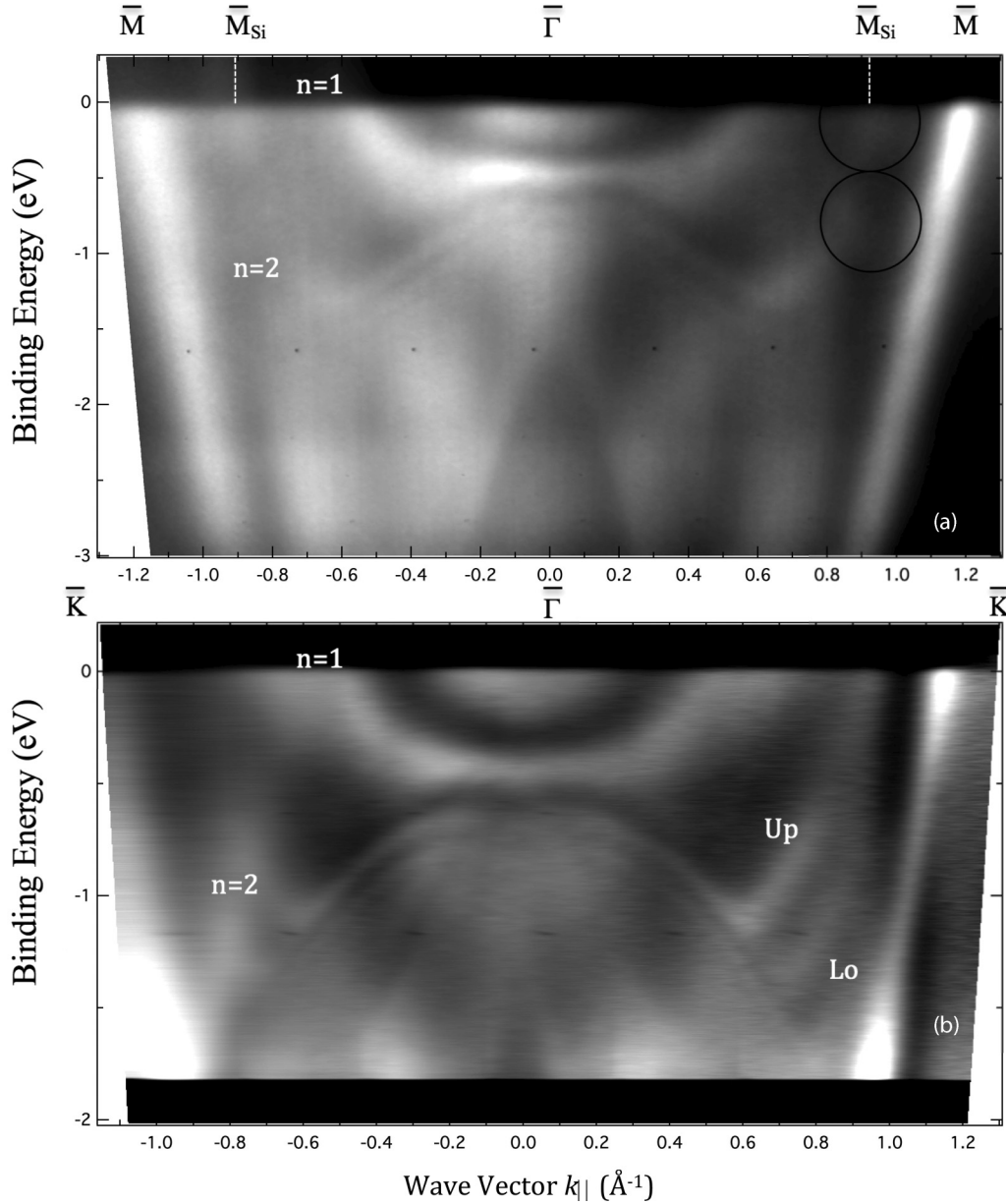


FIG. 1. Band structures of 4 ML Ag grown on Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ , recorded with a photon energy of 21.2 eV at 100 K. (a)  $\bar{\Gamma}$ - $\bar{M}$  direction. (b)  $\bar{\Gamma}$ - $\bar{K}$  direction.

level and disperses downwards to  $-0.6$  eV. Interestingly, this band seems to bend up again (kinks) and forms almost a plateau with a wiggle near the  $\bar{\Gamma}$  point. The second parabolic band ( $n = 2$ ) appears as a rather diffuse band. It starts  $-1.0$  eV at  $k_{\parallel} = \pm 0.85 \text{ \AA}^{-1}$ , and disperses downwards to  $-1.25$  eV at  $k_{\parallel} = \pm 0.65 \text{ \AA}^{-1}$ , then it quickly disperses upwards. In the zone center, these two quantum-well bands form wiggles and kinks that resemble the concave curves observed in the Ag/Ge(111) system and the electronic fringes observed in the Ag/Si(111) system [8,9,17].

In addition to the normal QWSs, there are also two resonance states dispersing downwards to the zone center in Fig. 1(a). When the two QWS bands approach the Si band edge, they break up from the fully confined QWS bands and appear as diffuse parabolic bands with minimum

energies of approximately  $-1.0$  and  $-2.6$  eV at the  $\bar{\Gamma}$  point. Looking closely, there are barely some intensities around  $k_{\parallel} = \pm 0.94 \text{ \AA}^{-1}$ , the  $\bar{M}$  point of the Si(111) SBZ, as indicated by two circles. These are two Umklapp QWSs, which appear even though the film is very thin. Besides, the strongest metallic bands at  $k_{\parallel} = \pm 1.25 \text{ \AA}^{-1}$  are the Ag  $sp$  bands, which cross the Fermi-level near the  $\bar{M}$  point of the Ag(111) SBZ. Because of the obvious interference from the Umklapp QWSs, the  $\bar{\Gamma}$ - $\bar{M}$ - $\bar{\Gamma}$  direction is thus not an ideal symmetry line to explore the fully confined QWS bands.

Figure 1(b) shows a valence band image along the  $\bar{\Gamma}$ - $\bar{K}$ - $\bar{M}$  line. Compared to the QWSs in Fig. 1(a), this symmetry line reveals much more details of the band dispersions and the coupling features. Near the  $\bar{\Gamma}$  point, the shadows (with extensions) in the  $n = 1$  band form the concave curves that

nearly resembles the heavy hole, light hole, and the spin-orbit split-off bands of the substrate. Approaching  $k_{\parallel} = \sim \pm 0.6 \text{ \AA}^{-1}$ , the  $n = 2$  band clearly bends up and follows with the Si bulk bands. Thus, it is clear that the inner part of the quantum-well state actually forms a coupling band, derived from the mixing of the quantum-well state and the Si bulk states. However, one puzzle is that there are two fully confined parabolic bands (Lo and Up branches) outside the Si zone edge, which have two turning points at  $(0.62 \text{ \AA}^{-1}, -1.125 \text{ eV})$  and  $(0.75 \text{ \AA}^{-1}, -1.375 \text{ eV})$ . Looking carefully, even the  $n = 1$  band shows a trace of double bands. The immediate question would be what causes the splitting? As demonstrated in Refs. [8,17], the QWS may split when a film thickness is not an integer number, which results in a nonuniform surface. In this context, one may suspect that the Lo branch could come from the  $n = 2$  band of a 3-ML film, and the Up branch may come from the  $n = 2$  band of a 4-ML film. However, a quantum-well state formed from such an extra-thin film has never been discussed before. Second, one would ask why the splitting is different in the two symmetry lines.

To verify what might be the cause, a theoretical study of the band structure was performed within the LAPW method of density functional theory. A slab consisting of 12 ML Si(111) representing the bulk, plus 3 ML Ag film on each side, with a lateral lattice using Si-bulk value and a vertical lattice using Ag-bulk value, was studied in the FLEUR implementation [18]. The consideration of this model is to laterally match with the well-defined Si(111) structure, but vertically match with the Ag film to form a standing wave. The 12-ML slab is chosen to ensure that the artificial coupling effect is very small between two sides of Ag films. Furthermore, Sn is also neglected in the calculation because Sn atoms play a very minor role since their chemical bonds are covalent and dangling bonds are very localized. Figure 2 shows an interesting result along two main symmetry lines. Starting from the  $\bar{M}$  and  $\bar{K}$  points, there are three double-split parabolic-shape bands that correspond to QWSs. Obviously, there is a clear difference between the  $\bar{\Gamma}$ - $\bar{M}$  and the  $\bar{\Gamma}$ - $\bar{K}$  direction. That is, the split ( $n = 2,3$ ) in the  $\bar{\Gamma}$ - $\bar{K}$  direction is much bigger

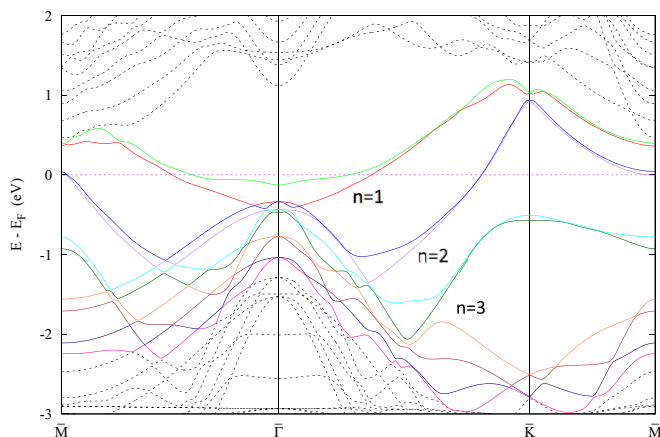


FIG. 2. DFT Calculation of the band structure. The model consists of a 12-ML slab plus 3 ML Ag film on each side, with a lateral lattice matching with Si and a vertical lattice matching with Ag. Various colors indicate different bands.

than the one in the  $\bar{\Gamma}$ - $\bar{M}$  direction. Approaching the zone edge, these QWS bands turn upwards and follow the Si bulk band dispersions. Interestingly, at the  $\bar{\Gamma}$  point the lower branch of the  $n = 1$  bands folds up and the upper branch of the  $n = 2$  bands first folds down and then up, creating a wiggle so that all the bands avoid crossing each other. Checking carefully, these turning points together with their upward curves form features that resemble the heavy hole, light hole, and the split-off bands of the Si substrate. They are the coupling state bands due to the mixing of the QWSs and the Si bulk states. Thus, the electronic fringes in Ref. [17] find an explanation in the calculation. Judged from the energy positions and shapes, the Lo and Up branches in Fig. 1(b) may originate from the split  $n = 2$  bands in Fig. 2.

On the other hand, the dispersions in the  $\bar{\Gamma}$ - $\bar{M}$  direction display very rich structures. Surprisingly, the discontinuity of the resonance state band ( $n = 1$ ) originates from various higher-order bands ( $n = 2,3$ ). For the  $n = 2,3$  bands, the calculations do not account for the resonance state bands all the way down to the minimum points. The bottom parts of the resonance states, however, could be derived from the strain-relaxed films, mostly from top layers, which are away from the interface and have more free-electron-like character. Therefore, the existence of the resonance states and the breaks points to a situation that the fully confined QWS may split. In fact, the above calculation implies an interface that has a finite thickness, which may lead to double reflections of the QWS band. However, since not all the structural details of the interface are known, more detailed calculations are much harder to perform. Recently, two stable surface structures have been found on Si(111) and Ag(111). One is a  $2 \times 2$  surface, which is formed with 1 ML Ag [referenced to Si(111)] plus  $2/3$  ML Sn on Si(111) [19]; another is a  $\sqrt{3} \times \sqrt{3}$  surface, which is formed with  $1/3$  Sn plus  $2/3$  ML Ag on Ag(111) [20]. In these two cases, the amount of top Ag atoms that bond with Sn is about 0.56–0.66 ML [referenced to Ag(111)]. In a simple picture, the interface itself thus should not be regarded as a complete monolayer of a Ag film. In the current system it was then estimated as a coverage of 0.56 ML since it should match the number of the Si atoms of the underlying substrate. Consequently, the “4-ML” film in Fig. 1 should actually have a coverage of 3.56 ML. Evidently, this noninteger thickness fits well with the observed QWS bands in Fig. 1, since the double-split QWS bands appear as a film with a half monolayer [17]. To conclude this part, both the valence spectra and the calculation indicate that the QWS bands have a natural split due to the existence of the interface, i.e., formed by the coupling of the QWSs with the substrate bulk states.

Figure 3(a) shows a valence band image recorded from a 13-ML Ag film along the  $\bar{\Gamma}$ - $\bar{M}$  direction. Located at  $-0.5$  to  $-1.5$  eV, there are coupling bands that disperse upwards and form a zone area, which divides the QWS bands into the fully confined and the resonance parts. Two resonance bands are clearly resolved with minimum energies located at approximately  $-0.6$  and  $-1.7$  eV. Six weaker Umklapp QWSs are found to center around the  $\bar{M}$  point of the Si(111) SBZ. Just looking at the parabolic bands ( $n = 1-4$ ), the thin Ag film appears to have a good quality since all the QWS bands are well-defined. However, as shown in Fig. 3(b), which is recorded along  $\bar{\Gamma}$ - $\bar{K}$  direction, the situation dramatically

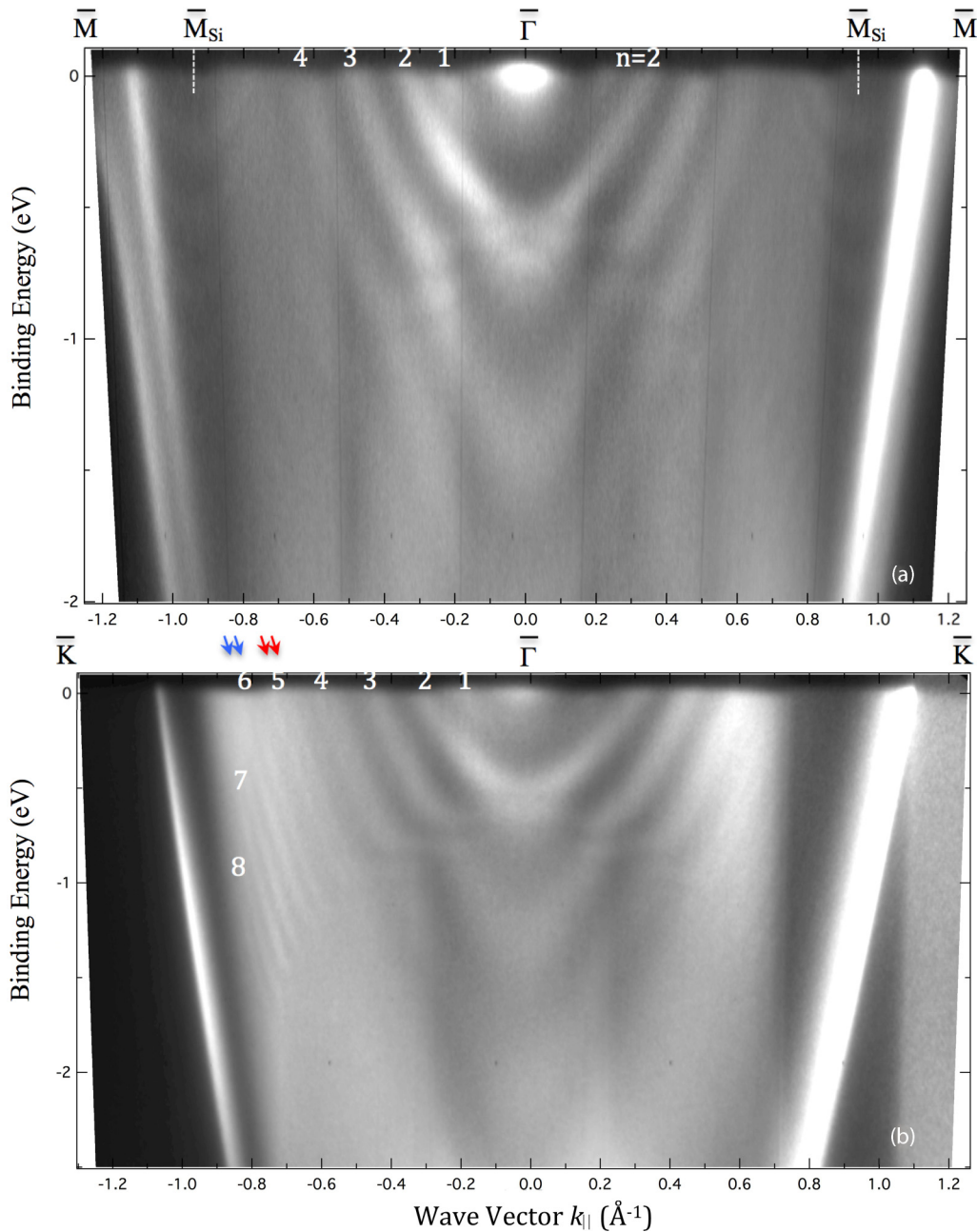


FIG. 3. Band structures of a 13-ML Ag film on  $\text{Sn/Si}(111)\sqrt{3} \times \sqrt{3}$ . (a)  $\bar{\Gamma}$ - $\bar{M}$  direction, recorded with a photon energy of 21.2 eV at 100 K. (b)  $\bar{\Gamma}$ - $\bar{K}$  direction, recorded with a photon energy of 40 eV at 100 K.

changes since the bands are doubly split again, especially for those with high quantum numbers ( $n = 5-7$ ). Note that the subband is well-resolved with a FWHM (full width at half maximum) of  $\sim 0.15$  eV. Assuming each band splits into two, then the total number of the bands will arrive at 16. Because this number is even larger than that of the Ag layers, these subbands cannot be the individual QWS bands. Furthermore, at the  $\bar{M}$  point of the Ag(111) SBZ in Fig. 3(a), even the Ag  $sp$  band is split into two. Switching to the  $\bar{\Gamma}$ - $\bar{K}$  direction as illustrated in Fig. 3(b), the Ag  $sp$  appears just as one bright band. Thus a split of the Ag  $sp$  band must be caused by the Umklapp scattering of Ag electrons with the Si(111) substrate.

The split in the fully confined QWS bands needs a thorough investigation. As mentioned above, if the actual film thickness

is not an integer, the QWS bands may show double-split subbands as demonstrated in Refs. [8,17]. To clarify this ambiguity, a set of images were converted from valence band spectra recorded from 12.5-, 13-, 13.5-ML films along the  $\bar{\Gamma}$ - $\bar{K}$  direction. As indicated by arrows in Fig. 4(a), on the two sides of the main bands ( $n = 4-6$ , indicated by the middle arrows), there are two split-off weak lines. Adding 0.5 ML Ag makes all the left lines disappear; while all the right lines gain significant intensities, which now equal to the main lines. As illustrated in Fig. 4(b), each QWS band thus has an upper and a lower branch (i.e., two branches) of the subbands. Adding another 0.5 ML Ag, a new line raises up at the right side of the upper branch, while the lower branch loses its intensity. In this way double bands in Fig. 4(b) become triple lines again, as shown



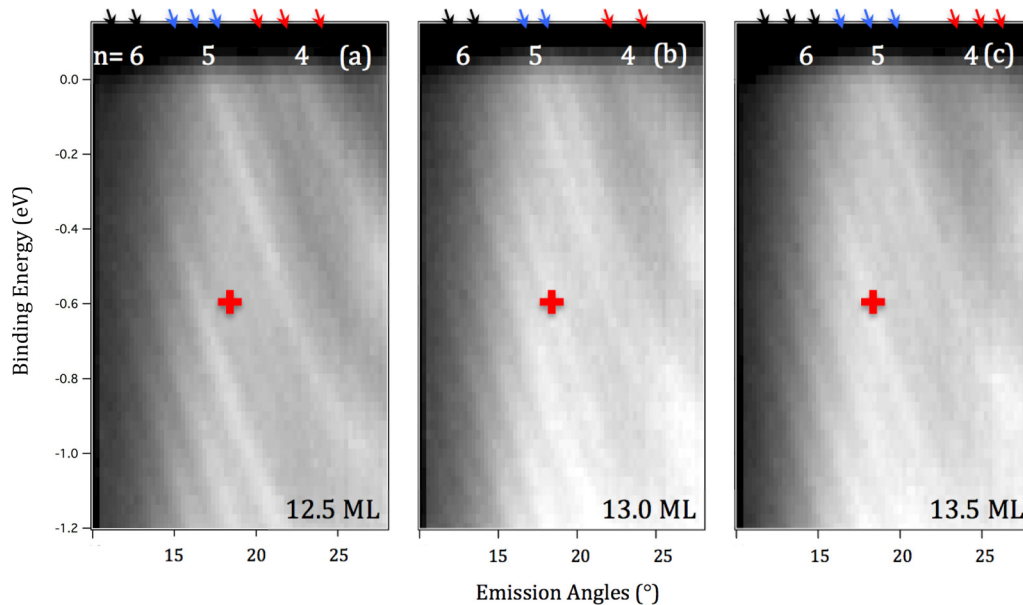


FIG. 4. Band structures of Ag films on  $\text{Sn/Si}(111)\sqrt{3} \times \sqrt{3}$ , recorded with a photon energy of 21.2 eV at 100 K, along  $\bar{\Gamma}-\bar{K}$  direction. The images were converted from valence band spectra around an emission angle of  $20^\circ$ . A red cross is for an eye guide to monitor the intensity variations of the QWS subbands. (a) 12.5-ML film, the  $n = 4-6$  bands are triply split as indicated by red, blue, and black arrows. (b) 13.0-ML film, the  $n = 4-6$  bands are doubly split as indicated by red, blue, and black arrows. (c) 13.5-ML film, the  $n = 4-6$  bands are triply split again, as indicated by red, blue, and black arrows.

in Fig. 4(c). Accordingly all the split subbands shift upwards to lower binding energies for higher coverages. There is no  $sp$  band splitting in the  $\bar{\Gamma}-\bar{K}$  direction, but in the  $\bar{\Gamma}-\bar{M}$  direction  $sp$  splitting does exist.

In our experiment, the surfaces with highest quality always show split QWS bands with almost equal intensities in the  $\bar{\Gamma}-\bar{K}$  direction. One can then consider a simple model that a film consists of 50%  $t$  and 50%  $t - 1$  monolayers of Ag with an equal growth rate. Adding 0.5 (0.3) ML extra Ag would result in 25% (15%)  $t + 1$ , 50%  $t$  (fixed), and 25% (35%)  $t - 1$  monolayers. Thus, the QWS band of the film should have triple lines because of three thicknesses. Adding 1.0 ML extra Ag would bring back double lines. One notices that in Fig. 2(B) of Ref. [17], diffused split bands appear as one after adding Ag, which the authors interpreted as two thicknesses. However, we found a clear evidence of double-triple-double behaviors of the QWS bands in the current system. On the other hand, for the thicker Ag films, one should expect the same growth mechanism, i.e., double-split bands should eventually become one by adding extra Ag. Thus, it is unlikely that double-thin lines of the QWS band in the current system come from a top surface with two thicknesses. Instead, a plausible scenario of the underlying physics of the split might originate from an interface. Its finite thickness could cause double reflections of the standing waves. Consequently, the reflections not only cause the energy shift of the QWSs in the normal direction but also cause the  $\bar{k}$  shift for the Umklapp scattering.

The value of the  $\Delta\bar{k}$  of the  $sp$  band splitting in Fig. 3(a) is  $\sim 0.081 \text{ \AA}^{-1}$ . One may assume the  $\bar{k}$  shift is roughly caused by a penetration of the electron wave into the interface for the Umklapp retroreflections. With a simple diffraction model, the estimated depth is approximately 1.85 ML of Ag. This value could be reasonable considering an interface that contains 1/3 ML Sn surrounded by 0.56 ML Ag plus one extra layer of Ag, which should match both sides of the interface. This agrees very well with the result of our calculation. Furthermore, as shown in Fig. 2, the split of the QWS bands increases with the quantum numbers of  $n$ . This could explain why the subbands are clearly resolved for the  $n = 5-8$  bands in Fig. 3(b).

In conclusion, high-resolution photoemission data of ultra-thin Ag films on  $\text{Sn/Si}(111)\sqrt{3} \times \sqrt{3}$  show intrinsic splitting of the quantum-well state bands. At a low coverage of 4 ML, the QWSs of such system display delicate coupling bands with the Si bulk states. The observed band splitting is more enhanced in the  $\bar{\Gamma}-\bar{K}$  than in the  $\bar{\Gamma}-\bar{M}$  direction. These results agree well with the theoretical calculation. At higher coverages, the  $sp$  band from the Ag film was also found to be split. Such a split is caused by the Umklapp scattering, which results in the  $\Delta\bar{k}$  shift. It is clear that all the splittings originate from an interface with a finite thickness. Our finding indicates the extra role of the interface that actually determines the electronic structures of the metal film on the semiconduct substrate.

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