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Substrate dependence of anisotropic electronic structure in Ag(111) quantum film studied by angle-resolved photoelectron spectroscopy

Taichi Okuda,* Yasuo Takeichi, Ke He, Ayumi Harasawa, Akito Kakizaki, and Iwao Matsuda
The Institute for Solid State Physics (ISSP), The University of Tokyo, Kashiwanoha 5-1-5, Kashiwa 277-8581, Japan

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Anisotropic quantum well states (QWS) of Ag(111) film fabricated on various one-dimensional superstructures on Si(111) substrate are systematically studied by angle-resolved photoelectron spectroscopy. It is found that Ag(111) epitaxial films can be grown on the Si(111)3×1-Ag, 5×2-Au as well as 4×1-In surfaces by the two-step growth method. Obvious anisotropic property of the QWS is observed only in the silver film on the Si(111)4×1-In substrate but not on the 3×1-Ag and 5×2-Au substrates. The difference of the anisotropy in the films on the various one-dimensional structures of Si(111) surface can be reasonably explained by considering the lattice mismatch between the fcc Ag(111) film and the superstructures underneath.

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Confinement of the electrons into nanoscale size, which is comparable to the electron wavelength, causes quantum size effect. Investigation of such a quantized effect is worthwhile not only for the fundamental understanding of the phenomena but for the application of such an effect to the future electronic devices. Quantum well state (QWS) in the metallic thin films is one of the examples of the quantum size effects and has been investigated extensively.[1–3]

It is suggested that the properties of the electronic structure can be modified or controlled by modulating the free-standing flat metal film by additional periodicity of the substrate or surface reconstruction. Such a modification of the band structure is called as electronic topological phase transition and predicted theoretically.[4] Recently such a modified QWS has been reported on the Ag(111) quantum films that were grown on GaAs(110) (Ref. 5) and Si(111)4×1-In (Refs. 6 and 7) surfaces. In the latter case, modulated film structure with a 4× periodicity of Si lattice vector has been observed by scanning tunneling microscopy (STM) (Ref. 6) and modulation of the electronic structure which shows one-dimensional property along the chain structure has been observed by angle-resolved photoelectron spectroscopy (ARPES).[7]

On the Si(111) it is well known that variety of superstructures can be fabricated by evaporating metals on the surface.[8] Among them, many surface reconstructions having one-dimensional chain structure with anisotropic electronic structure, like 3×1, 3×2, 4×1, 5×2, and so on have been reported by an evaporation of alkali metals, alkaline earth metals, noble metals, and rare earth metals on Si(111) surface.[8] These various kinds of one-dimensional superstructures provide a way to systematically study the influence of the substrate on the quantum well films and one may control the periodicity and/or anisotropy of the electronic structure of the QWS by choosing the optimum one-dimensional surface reconstruction as the template of the Ag epitaxial film.

Here, using the Si(111)3×1-Ag, 4×1-In, and 5×2-Au surfaces as the template of Ag film, the degree of one dimensionality of the in-plane dispersion of QWS has been systematically examined.

All the experiments were performed at the beamline BL-18A, Photon Factory, KEK, Japan. ARPES spectra were taken with VG-ADES 500 spectrometer at the sample temperature of 100 K. A vicinal Si(111) surface miscut in 1.8° toward $[\bar{1}\bar{1}2]$ was cleaned by direct current heating in a special heating procedure[9] to obtain uniform step structure which helps to fabricate single domain superstructure on the Si(111) surface. The single domain Si(111)3×1-Ag, 4×1-In, and 5×2-Au surfaces were fabricated by depositing Ag, In, and Au metals on the Si(111)7×7 clean surface at optimum temperatures[10–12] and checked by low-energy electron diffraction (LEED). Ag film was fabricated by so-called two-step growth.[13] Namely, Ag was evaporated on the substrates at about 100 K and annealed gradually up to room temperature. It is known that this two-step growth works well to obtain the Ag epitaxial films on semiconductor surfaces, such as clean Si(111),[3] Si(100),[3,13] Ge(111),[14,15] and GaAs(110) (Ref. 5) surfaces as well as on the Si(111)4×1-In surface.[6,7] The quality and the cleanliness of the films were confirmed by LEED pattern and x-ray photoemission spectroscopy as well as the Ag surface states observed in the ARPES spectra.

Figure 1 shows the ARPES spectra of Ag film with thickness of about 15 ML on Si(111)4×1-In taken at $h\nu = 21.2$ eV every one degree at both sides of the $\bar{\Gamma}$ point (thick spectrum). In (a), the ARPES spectra have been taken along parallel to substrate steps (see inset) which coincides with the chain direction of 4×1-In structure. On the other hand, in (b), spectra have been taken along perpendicular to the steps (i.e., perpendicular to the chain structure). These measurement directions correspond to the $\bar{\Gamma}$-$\bar{\mathrm{K}}$ and $\bar{\Gamma}$-$\bar{\mathrm{M}}$ symmetry lines of 1×1 surface Brillouin zone (SBZ) as indicated in the insets. A small peaks (**s**) near the Fermi level (dashed vertical line) at $\bar{\Gamma}$ point that are shown in both measurements are the so-called Shockley surface states of Ag (111) (Ref. 16) which is indicating that the film is well epitaxially grown. The other peaks in the spectra correspond to the QWSs. States with $n=1$ to 3 can be seen clearly in this thickness. In (a), QWSs show free electronlike parabolic in-plane dispersions. However, in (b) along the direction perpendicular to the chain structure, the parabolic dispersions are modified significantly. That is, the dispersions of QWSs become flat especially at around $\bar{\Gamma}$ point.

The modification of the parabolic dispersion is much more clearly seen in Figs. 1(c) and 1(d), which is the gray

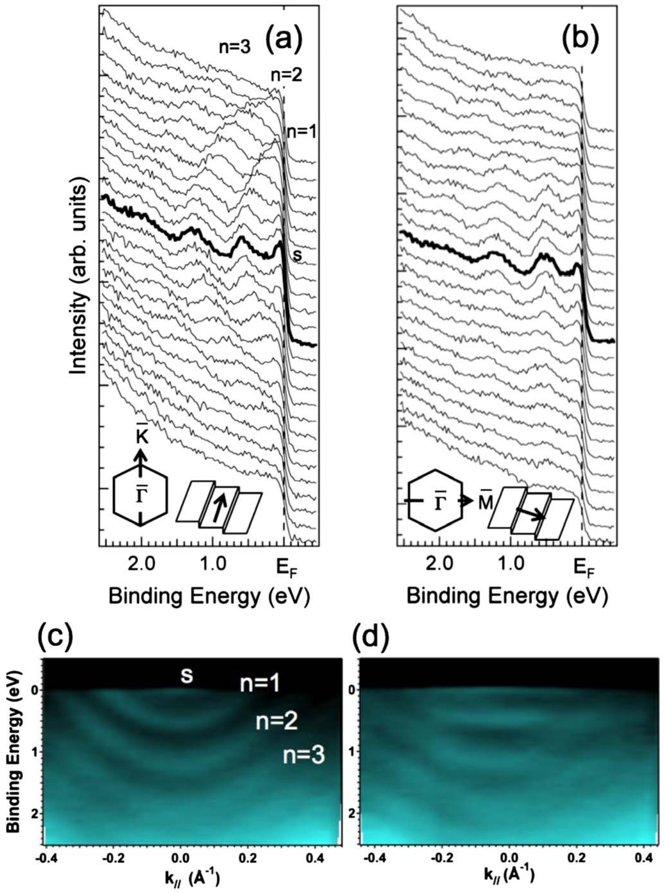

FIG. 1. (Color online) Angle-resolved photoelectron spectra of Ag thin film (~ 15 ML) on the single domain Si(111)4×1-In surface taken along the directions (a) parallel ($\bar{\Gamma}$-$\bar{\mathrm{K}}$) and (b) perpendicular ($\bar{\Gamma}$-$\bar{\mathrm{M}}$) to the surface steps with $h\nu=21.2$ eV. Small peaks (s) near the Fermi level (E_F) at around the $\bar{\Gamma}$ are so-called Shockley surface states of Ag(111). The gray scale band mappings from (a) and (b) are also indicated in (c) and (d).

scale band mapping obtained from the spectra in Figs. 1(a) and 1(b). In contrast to the nearly perfect parabolic dispersions along parallel to the chain structure, (c), the dispersions perpendicular to the chain structure, (d), are modified significantly and show almost flat dispersions at around the $\bar{\Gamma}$ point. These flat dispersions of QWSs are consistent with the previously reported ARPES results.[7] In the report, it was not clear if the dispersions are completely flat or not, since the observed k space was limited.[7] However, the present results show that at around $\bar{\Gamma}$ point the dispersions are flat but at higher wavenumbers they disperse upward. In addition, the dispersions are not completely symmetry against the $\bar{\Gamma}$ point and there are some discontinuities at the boundary between flat and upward dispersion parts. The boundary position roughly coincides with the $4\times$ folding of the SBZ ($k_{\parallel} \sim 0.23$ Å^{-1}). Therefore, the band structure shows some modification corresponding to the substrate periodicity. However, the electronic structure is not the complete one dimensional but rather anisotropic two dimensional. To observe the details of the complicated dispersion feature, however, high-energy and angular resolved ARPES measurement is required in the future.

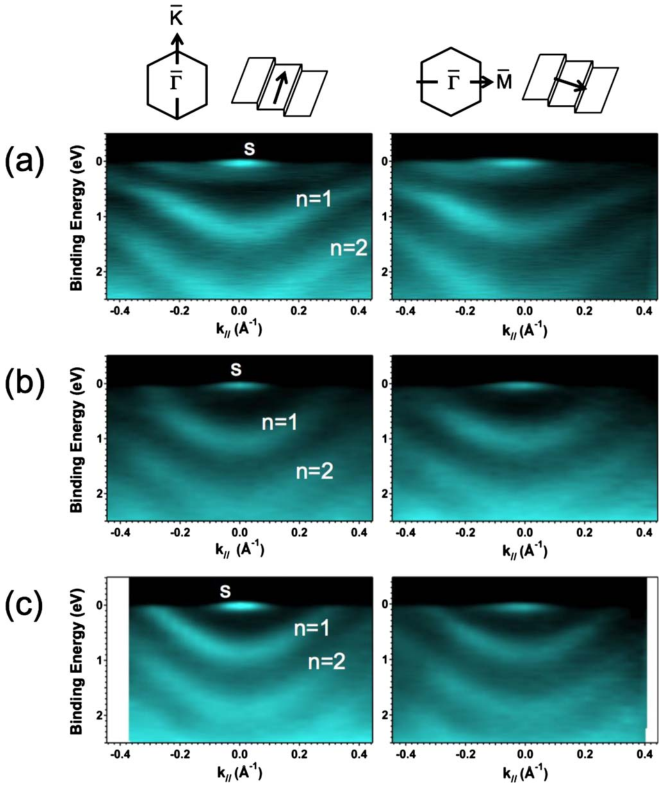

FIG. 2. (Color online) Gray scale band mappings of Ag films (~ 10 ML) on (a) Si(111)7×7, (b)3×1-Ag, and (c)5×2-Au substrates. Left panels are the band structures parallel to the chain structure (along step) of one-dimensional reconstructions of the substrate. Right panels are those perpendicular to the chain structure (perpendicular to the step). All the data were taken with $h\nu=21.2$ eV.

In Fig. 2, we show the band mapping of the Ag films on (a) Si(111)7×7 clean surface, (b) 3×1-Ag, and (c) 5×2-Au surfaces. As in the figure, all the films show clear QWS as well as Ag Shockley surface state (**s**) indicating the good quality of the Ag films. Thus, the results show that Ag epitaxial films can be grown by the two-step growth[13] on the Si(111)3×1-Ag, and 5×2-Au surfaces. Generally, the different electronic and/or atomic structures cause the different surface energy and/or bonding manner and can influence the growth mode of the film. However, in spite of the different surface reconstructions and the electronic properties; 3×1-Ag with semiconducting character,[17] 5×2-Au with complex electronic structure and weak metallic surface states,[18] and 4×1-In with one-dimensional metallic states accompanied by the charge-density wave transition,[19] the qualities of the epitaxial films are surprisingly similar.

Here, we would focus on the anisotropy of the QWS band dispersion on the Ag films on the different one-dimensional structures. Contrast to the case of the Ag film on the 4×1-In surface, the observed dispersions of the films with the thickness of ~ 10 ML on (b) 3×1-Ag and (c) 5×2-Au surfaces have free-electronlike parabola shapes even along the perpendicular direction to the chain structure and no obvious modification corresponding to the SBZ of the substrate superstructures ($k_{\parallel} \sim 0.31$ Å^{-1} for 3×1 and ~ 0.19 Å^{-1} for 5×2) was observed. If we compare the effective mass, slight

TABLE I. Observed effective masses of QWS ($n=1$ and $n=2$) of Ag films on 7×7, 3×1-Ag, 4×1-In, and 5×2-Au substrates along parallel and perpendicular to the step direction. The ratios of effective masses between parallel and perpendicular to the step direction are also shown.

	$n=1$			$n=2$		
	$m_\parallel^*/m_e$	$m_\perp^*/m_e$	$\frac{m_\perp^*}{m_\parallel^*}$	$m_\parallel^*/m_e$	$m_\perp^*/m_e$	$\frac{m_\perp^*}{m_\parallel^*}$
7×7	0.55 ± 0.04	0.66 ± 0.07	1.20	0.45 ± 0.05	0.46 ± 0.02	1.02
3×1	0.55 ± 0.05	0.67 ± 0.05	1.22	0.42 ± 0.04	0.46 ± 0.07	1.10
4×1	0.27 ± 0.03			0.38 ± 0.03		
5×2	0.36 ± 0.03	0.45 ± 0.04	1.25	0.41 ± 0.02	0.58 ± 0.09	1.41

increase is observed in the QWS bands perpendicular to the chain both on the 3×1 and 5×2 surfaces as in Table I. The effective masses perpendicular to the chain structure in the Ag film on the 3×1-Ag surface are about 10%–22% larger than those of parallel to the chain. In case of the film on the 5×2-Au, the increment is ~25–40%. However, even in the QWS of Ag film on the 7×7 in which the film is quite homogeneous, similar increase in the effective mass is observed in the QWS perpendicular to the step ($\bar{\Gamma}$-$\bar{\text{M}}$ direction) compared with that of parallel to the step ($\bar{\Gamma}$-$\bar{\text{K}}$) as in Table I. It is likely that the dispersions along different symmetry lines ($\bar{\Gamma}$-$\bar{\text{M}}$ and $\bar{\Gamma}$-$\bar{\text{K}}$) have different effective masses even in the homogeneous film. The other possibility is that the Si(111) substrate used here is a vicinal sample and the step may cause a little larger effective mass of the QWS band dispersion along the direction perpendicular to the step. Comparing the increase in the effective mass in the films on the one-dimensional structures with that of on the 7×7 surface, the film on the 3×1-Ag is almost homogeneous and that on the 5×2-Au is only slightly anisotropic.

Recently, Uchihashi *et al.*[6] proposed the structural model for the modified Ag film on the Si(111)4×1-In surface on the basis of their STM observation. In the model, because of the lattice mismatch between fcc Ag(111) and 4×1 reconstructed Si surface, a stacking fault is presented in the ideal fcc structure of Ag film every five silver stacking to reduce the lattice mismatch. Figure 3 illustrates the situation. The gray circles representing the Ag atoms are superimposed on the Si primitive lattice which is illustrated as the hexagon sheet. Dashed (red) rectangles show the size of the substrate reconstructions. As shown in Fig. 3(b) in case of 4×1 substrate, by introducing one stacking fault [(green) vertical dashed line], the original lattice mismatch can be reduced effectively. That is, by presenting one stacking-fault the transversal size of silver film (~12.88 Å) matches well with that of substrate reconstruction (~13.30 Å) and the lattice mismatch reduces from 6% to 3.2%. Therefore, presenting one stacking-fault every five Ag stacking likely occurs in case of the Si(111)4×1-In substrate. Electron confinement or band folding perpendicular to the chain structure by generated uniform periodic potential causes the anisotropic band structure in the film.

On the other hand, in case of 3×1, the matching of the transversal sizes of substrate reconstruction and the Ag(111) film is almost perfect by nature as shown in Fig. 3(a). The mismatch is only 0.3% and it is not necessary to introduce any stacking fault to grow an uniform Ag film on the substrate. Since the film is quite homogeneous, the electronic structure of QWS must be also homogeneous and no obvious anisotropy of band dispersions between parallel and perpendicular to the chain structure of 3×1 is observed.

In case of the 5×2 substrate, the situation is different. Since we are considering the lattice mismatch along $n\times$ periodicity, the unit cell of 5×1 instead of 5×2 is considered for the simplicity in the following discussion. As in Fig. 3(c), the original mismatch between the fcc Ag film and the 5×1 unit is about 5% which is in between 3×1 and 4×1 cases. Because of this moderate mismatch, even if one stacking fault is introduced the mismatch is not reduced effectively. We show the situation in Fig. 4. As in Fig. 4(a), one stacking fault gives rise to larger lattice mismatch than that of without stacking-fault. Even with two stacking-faults [Fig. 4(b)], still the lattice mismatch is almost the same to that without a stacking fault. With three stacking faults [Fig. 4(c)]

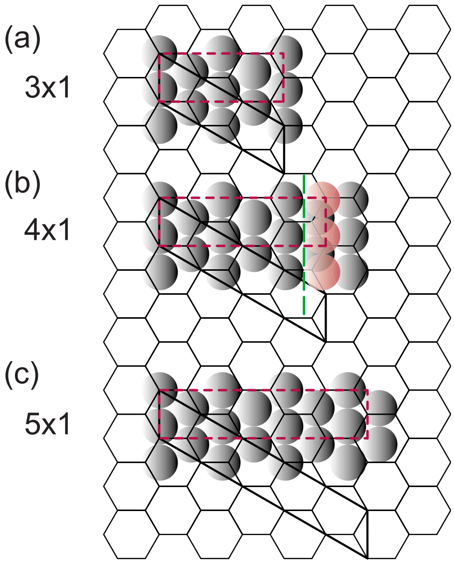

FIG. 3. (Color online) Schematic diagram of the register of Ag(111) film on the reconstructed Si(111) surfaces. Gray circles represent the position of Ag atoms and hexagons are the places of Si(111) substrate. Rhombuses are the unit cells of superstructures, (a) 3×1, (b) 4×1, and (c) 5×1. Dashed (red) rectangles are the sizes of the unit cells of these superstructures. In case of (b) 4×1, one stacking-fault [(green) dashed vertical line] reduces the mismatch effectively.

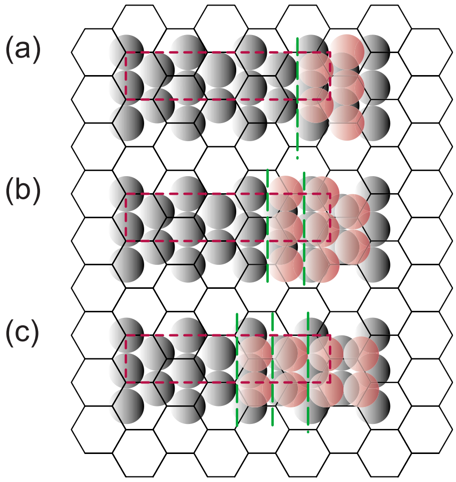

FIG. 4. (Color online) Schematic view of the effect of introducing stacking-faults [(a) one stacking-fault, (b) two faults, and (c) three faults] in the Ag film on 5×1 substrate. Until introducing three stacking faults, the matching of the Ag film, and the substrate superstructure is not improved.

the mismatch reduces to about 3% which is comparable to the case of the Ag film on 4×1-In surface. In case of the silver, the energy to introduce stacking fault ($\equiv$ stacking-fault energy) is smaller by factor of 2 to 3 than those for the other noble metals or by order of magnitude than those for other transition fcc metals.[20] However, many stacking faults causes higher total energy even though the stacking-fault energy is small and the system will be unstable. Therefore, in case of $5\times$ periodicity, the gain of making stacking fault is small and the film does not have the structure with uniform stacking faults in reality. In consequence, stacking faults or defects can be introduced randomly to relax the instability and the film becomes relatively homogeneous. The other possibility is that the moderate mismatch gives rise to the film with homogeneous strain. Smaller effective mass in the film on the 5×2-Au than those on the 3×1-Ag or 7×7 may imply the compressed Ag film by the strain. Further experimental and theoretical investigations are expected to reveal the relation between the film structure and the electronic states in detail. The missing of the anisotropy in the band dispersion of the films on the substrates with 3×1 and 5×2 periodicities, however, is the collateral evidence of the validity of the stacking-fault model as the silver structure on the 4×1-In surface.

In conclusion, we have investigated the substrate dependence on the anisotropy of electronic structure of QWS in the Ag thin film. It is found that the epitaxial Ag(111) films can be grown on the Si(111)3×1-Ag, 5×2-Au as well as the 4×1-In by so-called two-step growth. Only the superstructure of Si(111) having 4×1 periodicity can be a effective template which causes the anisotropy of band dispersions in the Ag(111) film. However, on the superstructures with other periodicity such as 3×1 or $5\times 1(2)$, the QWS bands show free-electronlike parabolic dispersions. These substrate dependence on the anisotropy of the QWS band structure in the Ag film can be understood by considering the matching of the Ag fcc lattice and the one-dimensional structure underneath. These results suggest that one can control or design the dimensionality of electronic structure of QWS by considering the size mismatch between unit cell of the substrate superstructure and the overlying film structure. In order to confirm this scenario, STM observation of Ag film on the substrates with different one-dimensional periodicities is expected.

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*Present address: Hiroshima Synchrotron Radiation Center, Hiroshima University, Kagamiyama 2–313, Higashi-Hiroshima 739–0046, Japan; okudat@hiroshima-u.ac.jp

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