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Electromigration and phase transformation of Ag on a Cu-precovered Si(1 1 1) surface

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Abstract

Electromigration and phase transformation of an ultrathin-Ag film patch deposited on a Cu-precovered incommensurate "5 × 5" phase on Si(1 1 1) surface were investigated by in situ ultrahigh-vacuum scanning electron microscopy and microprobe reflection high-energy electron diffraction, and compared with the previous results on the clean and Au-precovered Si(1 1 1) surfaces. The film patch spread quite slowly towards the cathode by current apply (and resultant heating), at the initial stage of which the patch area showed a $\sqrt{3} \times \sqrt{3}$ phase, consisted of Ag–Cu surface alloy, with three-dimensional (3D) islands in it. Later, a phase transformation from the $\sqrt{3} \times \sqrt{3}$ into a $\sqrt{21} \times \sqrt{21}$ structure proceeded, accompanied with the 3D islands dissolving. These surface alloy formations play a key role in the migration, which is similar to the case of on Au-precovered Si(1 1 1) surfaces. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, a directional mass transport of ultra-thin metal films (up to several monolayers in coverage) deposited on Si(1 1 1) or Si(1 0 0) substrates, which is induced by applying direct current across the substrate, referred to as surface electromigration, has attracted more attention in view of the fundamental and technological significances [1].

An idea was proposed to employ such electromigration for the formation of the first atomic metal layer in direct contact with the semiconductor surface in fabrication technology [2]. The interface formed in this way is expected to be almost free from structural defects that have crucial influence on the electrical properties of metal/semiconductor contacts. Since it was first found through a reflection high-energy electron diffraction (RHEED) experiment of In/Si(1 1 1) system [3], several groups [4–17] have systematically studied this phenomenon. The topics of interest include migration preferential direction, diffusion kinetics, and influence of steps, adsorbed surface structure changes, as well as single domain structure formation of various metals on Si(1 1 1) and Si(1 0 0) surfaces. Among

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them, the electromigration of noble metals is of special interest and has been intensively studied. The electromigration characteristics were found to show different features depending on the species. It is known that Au moves towards the anode side on clean Si(1 1 1), while Ag and Cu moves towards the cathode side [9]. It is also known that the above-mentioned metals cause different reconstructed surface structures on Si(1 1 1) [18].

In spite of these studies, electromigration of the same metal on differently modified surfaces is seldom reported. In our previous paper [19], we have studied Ag electromigration on Au-precovered Si(1 1 1) surfaces, revealing a strong dependence of the migration behavior on the Au coverage. The phenomena were systematically understood by a rule that the deposited Ag-film patch spreads to attain a final two-dimensional (2D) alloy where the total coverage of Ag and Au is always one monolayer (ML) irrespective of Au/Ag coverage ratios. In another paper [20], we compared the electromigration behaviors between Ag and In on the Au-precovered Si(1 1 1) surfaces; quite different behaviors between the two species were attributed to different surface alloy phases between Ag–Au and In–Au formed during migration. In this paper, we applied similar observations with in situ scanning electron microscopy (SEM)–RHEED to study electromigration of Ag on Cu-precovered Si(1 1 1)-"5×5" incommensurate phase, and compare the results with the cases of clean and Au-precovered Si(1 1 1) substrates. It was found that a transformation of alloy phases from $\sqrt{3} \times \sqrt{3}$ to a $\sqrt{21} \times \sqrt{21}$ plays a crucial role.

2. Experimental

An ultrahigh-vacuum field-emission SEM and microprobe RHEED apparatus (customized Hitachi S-4200), connected to a molecular beam epitaxy chamber for in situ deposition, was used, details of which was described in Ref. [20]. The substrates used ($15 \times 3 \times 0.4$ mm^3 in size, 50–100 Ω cm in resistivity) were cut from an n-type mirror-polished Si(1 1 1) wafer with its longer side parallel to $\langle 1 \bar{1} 0 \rangle$ direction. The substrate were inserted into the

chamber without any prior chemical etching, mounted on a pair of tantalum clamps of the sample holder, and cleaned by resistive heating above 1473 K to obtain a clear 7×7-RHEED pattern. In the present experiments, the substrate temperature was controlled only by feeding direct current, so the current and sample temperature could not be changed independently. First, Cu of ~1.5 ML was deposited on the whole substrate surface of clean 7×7 structure at 773 K to form an incommensurate "5×5" surface phase on the entire surface. The coverage of the metal deposits used here are expressed in monolayer, a monolayer refers to 7.8×10^{14} atoms/cm^2. Next, deposition of Ag was made at room temperature on the "5×5"-Cu surface through a slit of ~150 μm wide to get a reproducibly defined rectangular film patch on the center of substrate. Spreads of the Ag film patch caused by applying constant direct current (and resultant heating) were observed in situ by SEM. The surface superstructures inside and outside of the Ag film patch were determined by microprobe RHEED. Grazing-incidence SEM observations and RHEED measurements were in situ done before, during, and after the current stressing. The acceleration voltage of the electron beam was 30 kV, the glancing angle of the beam was about 10° from the surface in SEM, and the beam diameter was about 2 nm on the sample surface.

3. Results and discussion

A series of SEM images are reproduced in Fig. 1 to show the electromigration of a Ag film patch on the Si(1 1 1)-7×7 clean surface (a) and (b) and "5×5"-Cu surface (c)–(e). Fig. 1(a) and (c) represents the as-deposited Ag film patches with nominal coverage of 3.7 ML, and Fig. 1(b), (d) and (e) shows the situations of the patch after direct current (0.42 and 0.49 A, respectively) stressing for (b) and (d) 10 min and (e) 30 min, respectively, at 813 K. Preferential expansions of the patch towards the cathode are noted on both substrates during the current stressing although backward spreads towards the anode are also seen, due to thermal migration. However, the migration speed and expanding speed of Ag patch in (d) and (e) were
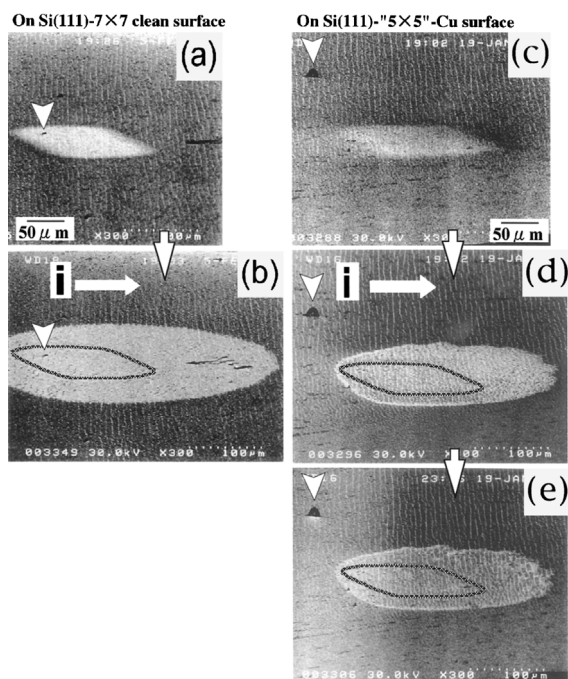
On Si(111)-7×7 clean surface   **On Si(111)-"5×5"-Cu surface**

Fig. 1. A series of SEM images showing the electromigration of a Ag film patch on the 7×7 clean surface (a), (b) and on the incommensurate "5×5"-Cu phase (c)–(e) on Si(1 1 1) surface. (a), (c) As-deposited Ag film patch. (b) Ag patch of (a) after direct current ($I = 0.42$ A, $T = 813$ K) flowing along the horizontal direction in this image for 10 min. After electromigration for (d) 10 min and (e) 30 min, with $I = 0.49$ A at $T = 813$ K. The silicon carbide indicated by arrowheads in each image can be used as a marker to evaluate the migration distance. The shape and location of the initial patches are traced in (b), (d) and (e).

much lower than in (b) (and also lower than on the Au-precovered Si(1 1 1) surfaces less than 0.7 ML [19]). The patch area showed a $\sqrt{3} \times \sqrt{3}$-RHEED pattern at the initial stage of migration, meaning a 2D-alloy phase of Ag and Cu (and also Si) which is denoted by $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) hereafter. On the 7×7 clean substrate, the patch area is the $\sqrt{3} \times \sqrt{3}$ phase composed of Ag only, known as a honeycomb-chained triangle (HCT) structure [21]. In Fig. 1(d), slight difference in brightness can be found between the front part (right side) and rear part (left side) of the Ag patch, while at a later stage, as shown in Fig. 1(e), such a difference almost disappears (i.e., almost uniformly darker). This change corresponds to a phase transformation occurred in the Ag film patch, as described

below. On the 7×7 clean substrate, as shown in Fig. 1(b), on the other hand, such a contrast is not seen in the patch area where only the $\sqrt{3} \times \sqrt{3}$-Ag phase of the HCT structure develops [21].

Fig. 2(a) was taken inside the Ag patch after electromigration on the "5×5"-Cu surface after 1 min of current applying. Three-dimensional (3D) islands were seen on terraces and near edges of step bands. Larger islands tend to have round shapes, while smaller islands have flat tops. Quite similar to the case of Ag on the Au-precovered surfaces [19], the Ag islands are immobile during current applying. Instead, they just dissolve into substrate and
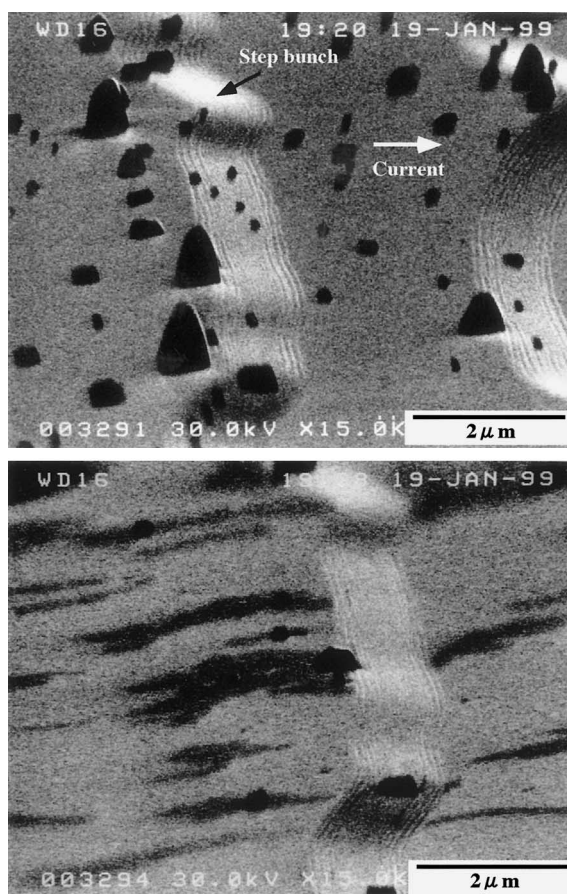

Fig. 2. SEM images in the Ag film patch during electromigration on the Si(1 1 1)-"5×5"-Cu surface. (a) After 1 min and (b) 5 min with $I = 0.49$ A at $T = 813$ K. Dark regions in (b) represent the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase, while the rest parts with higher brightness represents the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) phase.

form a Ag–Cu 2D phase as observed by darker regions in Fig. 2(b) (after 5 min of electromigration at the same region as in (a)). From microprobe RHEED measurements and scanning reflection electron microscopy observations, it was determined that the darker and brighter regions in Fig. 2(b) were the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) and $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) surface phases, respectively.

Fig. 3 shows another example of the phase transformation during Ag migration on the "5 × 5"-Cu surface. The upper row ((a)–(c)) and lower row ((d)–(f)) describe separate series of evolution details of islands dissolving and the simultaneous growth of the $\sqrt{21} \times 21$-(Ag + Cu) domains (dark regions). It seems that some atoms are detached from the elongated 3D islands, causing the formation and expansion of the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase on the terraces.

Fig. 4(a) shows the surface at the front edge (cathode side) of the Ag patch, after 10 min of electromigration on the "5 × 5"-Cu surface. Darker regions on the right are the "5 × 5"-Cu phase, while brighter regions on the left area having the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) structure. Thus, at the very front edge, the patch area is only the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu)

phase. But at the inner region of the patch, some minor portions are the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase, immersed in the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) major domains, as shown in Fig. 4(b). Near the rear edge of the Ag patch, as shown in (c), the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase is the major. Thus the surface structure is not uniform across the patch, which correspond to the non-uniform brightness across the patch observed in Fig. 1(d). The $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase grows also near the front edge by longer current stressing. These observations indicate that the expansion of the patch proceeds in a way that the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) phase (bright domains) first spreads on the "5 × 5"-Cu surface and then it transforms into the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) structure later. Such a transformation begins preferentially from near the rear edge (anode side). This is probably because a gradient in Ag concentration occurs across the patch.

Then combined with the results in Figs. 1–4, the process of Ag electromigration on this surface is summarized as schematically shown in Fig. 5. The patch forms the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) alloy phase first, acting as a leading phase for electromigration (Fig. 5(b)). Excess Ag and Cu atoms form
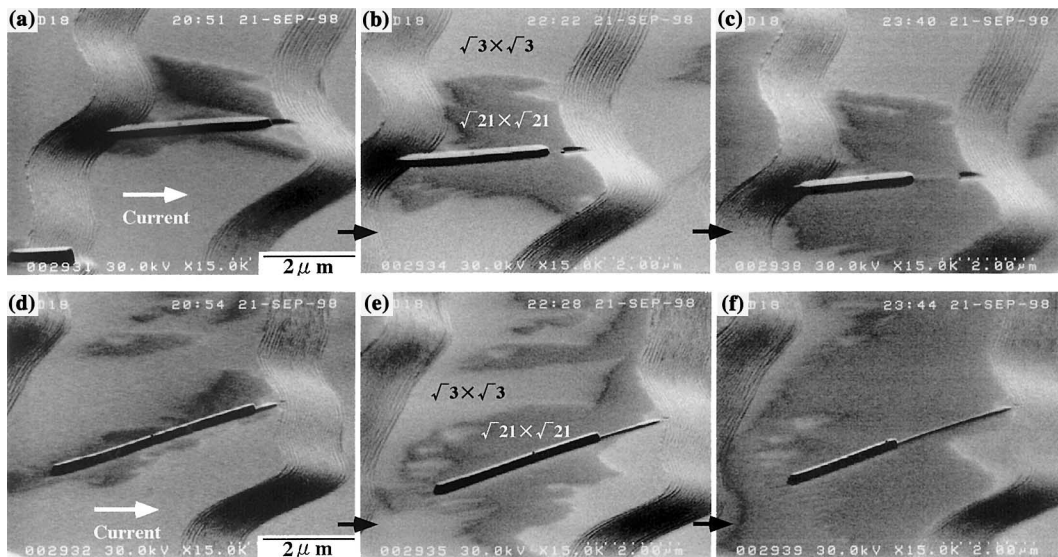

Fig. 3. Two series of SEM images ((a)–(c) and (d)–(f)) showing the details of 3D islands dissolving into the substrate and accompanied growth of the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) domains on terraces inside the Ag film patch during electromigration on the "5 × 5"-Cu surface. (a), (d) After 5 min 30 s, (b), (e) 11 min, and (c), (f) 22 min. Dark regions in each images represent the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase and brighter ones are the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) phase. $I = 0.53$ A, $T = 813$ K.
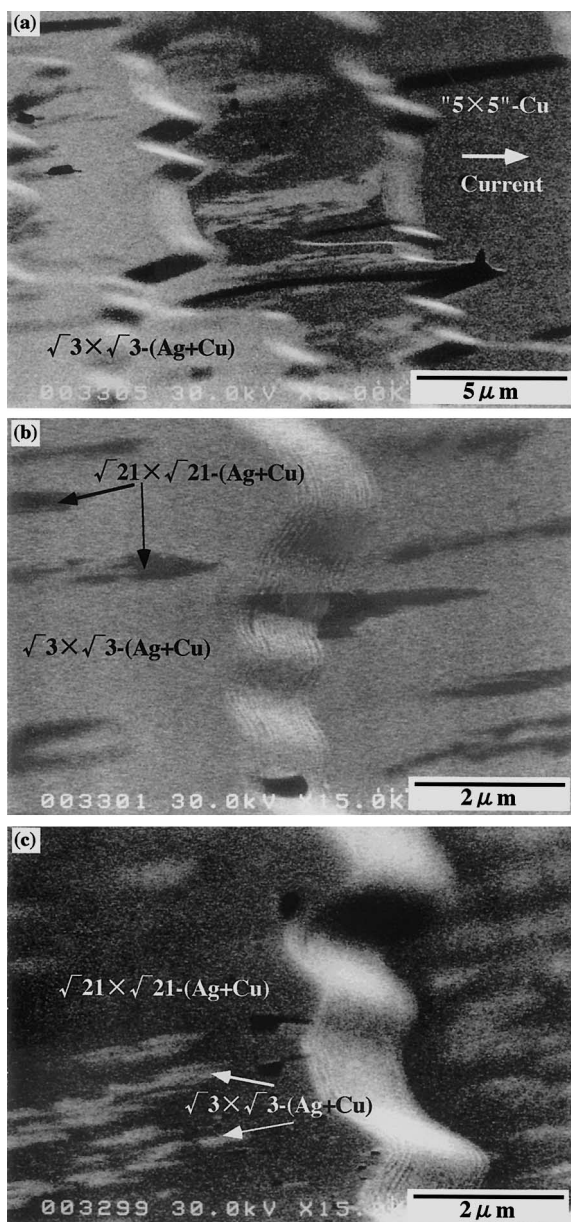
Fig. 4. SEM images taken after electromigration for 10 min with $I = 0.49$ A at $T = 813$ K. (a) At the front edge of the patch, (b) inside the patch near the front edge, and (c) inside the patch near the rear edge, showing different distributions of the $\sqrt{21} \times \sqrt{21}$ and $\sqrt{3} \times \sqrt{3}$ phases across the Ag film patch along the current direction.

Fig. 5. Schematic illustrations of electromigration of a Ag-film patch on the Si(1 1 1)-"5 × 5"-Cu surface.

$\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase continuously, accompanied with dissolving the 3D islands into the substrate (Fig. 5(c)). This transformation results in the further expansion of the patch (Fig. 5(d)). The $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase should be more Cu-rich than the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) phase in this model.

Fig. 6(a) and (b) are inside the patch area after 5.5 and 11 min of electromigration, respectively, showing a special morphology feature during electromigration. The areas in close vicinity to the 3D islands are denuded, suggesting that the substrate Si atoms are extracted and incorporated into the 3D islands. The denuded hollows tends to expand preferentially on the cathode side of the 3D islands. Intermixing of Cu and Si atoms at Cu/Si(1 1 1) interface was observed by RHEED intensity oscillation studies at low and high temperatures [22,23].

3D islands. By decreasing Ag concentration near the rear edge of the patch by electromigration, the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) phase transforms into the
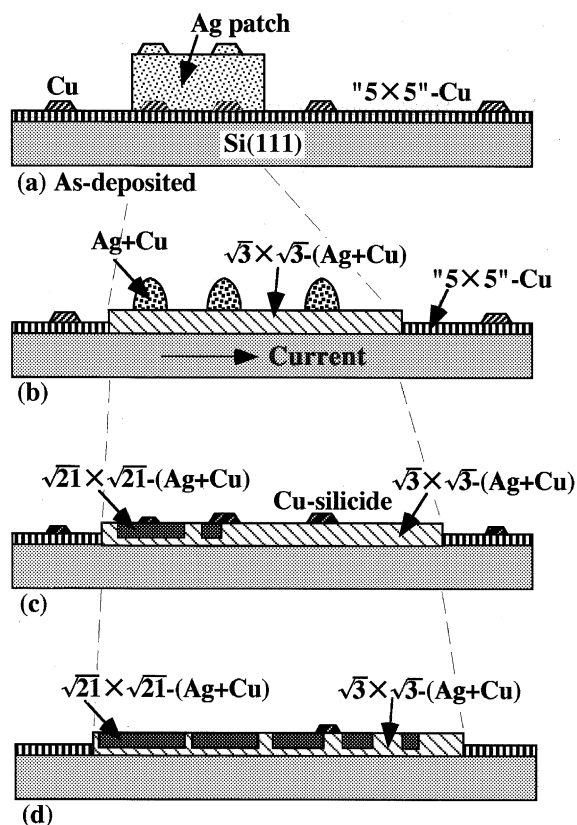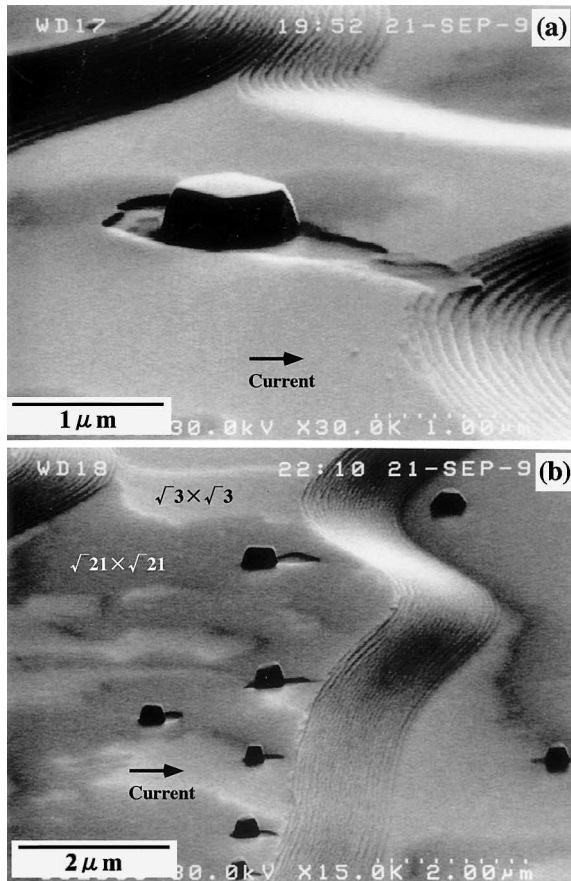
Fig. 6. Denuded hollows accompanying 3D islands during electromigration of Ag on the "5 × 5"-Cu surface. $I = 0.53$ A, $T = 813$ K. (a) 5 min 30 s, (b) 11 min. Bright regions on a terrace are the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) phase, while darker regions are the $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase.

However, the electromigration of the single species of Ag or Cu do not show any denuded hollows on the clean Si(1 1 1) surface [19,20]. Therefore such morphology feature is observed only in this Ag–Cu bimetal system. On the initial stage of electromigration such as shown in Fig. 2(a), the 3D islands do not accompany such denuded hollows. The hollows appear only on the later stage at some places where the 3D islands dissolve and $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase appears in the $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) domains. So the formation of hollows is supposed to be related to a change of Si atom density at the phase transformation from the $\sqrt{3} \times \sqrt{3}$ to the $\sqrt{21} \times \sqrt{21}$.

A $\sqrt{21} \times \sqrt{21}$ superstructure is known to appear by small amounts of Cu deposition onto the $\sqrt{3} \times \sqrt{3}$-Ag surface of the HCT structure [24] at room temperature. Its RHEED pattern is quite similar to the present $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) phase that should be more Cu-rich. Although it is not clear at the moment whether their atomic arrangements are the same or not, the $\sqrt{21} \times \sqrt{21}$ structures may be alloy phases with different concentration ratios between Cu and Ag. Such a 2D-alloy phase formation and its decisive role in electromigration behaviors are quite similar to the Ag case in Au-precovered Si(1 1 1) surface [19].

4. Summary

By using in situ SEM and microprobe RHEED observations, we investigated the electromigration behaviors of a Ag film patch deposited on an incommensurate "5 × 5"-Cu phase on Si(1 1 1) surface. It was found that the patch area showed a $\sqrt{3} \times \sqrt{3}$-(Ag + Cu) 2D-alloy phase first as a leading phase with 3D islands on it, and later it transformed into $\sqrt{21} \times \sqrt{21}$-(Ag + Cu) 2D-alloy phase, accompanied with 3D islands dissolving. Such a phase transformation occurs first near the anode side (rear edge) inside the patch, and expands towards the cathode side (front edge) across the patch, which results in the patch expansion. This indicates that Ag atoms migrate towards the cathode inside the patch, causing its concentration gradient across the patch.

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