Diffusion anisotropy of Ag and In on Si(1 1 1) surface studied by UHV-SEM

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Received 19 March 1999; received in revised form 6 March 2000

Abstract

Anisotropic features of Ag and In electromigration on clean and Au-precovered Si(1 1 1) surfaces were studied by in situ scanning electron microscopy in ultrahigh vacuum. It was noted that the migration direction of Ag was determined by both applied direct-current direction and step orientation on the substrate surface; on an Si(1 1 1) surface with steps inclined with respect to the current direction, the electromigration direction shows an apparent deviation from the accurate current direction. On clean and Au-precovered Si(1 1 1) surfaces with various coverages of Au (within submonolayer range), the migration behaviors of Ag and In drastically changed with Au coverages and showed different diffusion anisotropy (either thermal diffusion and electromigration) depending on the adsorbate surface structures. Particularly, on a $\sqrt{3}\times\sqrt{3}$-Au surface of one monolayer Au coverage, In migrated with the highest mobility across the step bands, whereas In showed only a slow movement on the $7\times7$ clean surface due to a migration barrier at step edges. This result implied that the $\sqrt{3}\times\sqrt{3}$-Au surface phase served as an intermediate layer for In adatoms migration. On the contrary, Ag showed negligible migration on the $\sqrt{3}\times\sqrt{3}$-Au surface, while the $7\times7$ surface was the substrate for appreciable migration of Ag atoms. The results are discussed in terms of step-edge barriers in migration and on-terrace migration.

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PACS: 66.30.Q; 61.16.B; 68.35.F; 73.50

Keywords: Electromigration; SEM; Diffusion anisotropy; Indium; Silver; Au/Si superstructures; Intermediate layer

1. Introduction

Surface diffusion is a physically interesting process and also technologically important since it affects many physical and chemical properties \cite{1,2} such as crystal growth, electrical conduction, catalysis, and adsorption. Therefore, surface diffusion has been intensively investigated using a variety of techniques \cite{3,4,5,6,7,8}, both microscopy and spectroscopy. As a good example of surface diffusion, the movement of ultrathin foreign metal films on semiconductor surfaces induced by a direct-current heating in ultrahigh vacuum (UHV) condition is referred to as surface electromigration. It was first reported by Zhou et al. with reflection high-energy electron diffraction...
(RHEED) experiment [9]. Later, this interesting phenomenon was studied in detail by Yasunaga et al. [10–16] using scanning Auger microscopy (SAM) and by Yagi et al. [17–22] using reflection electron microscopy (REM). The UHV scanning electron microscope (SEM) is also a powerful tool to study the surface dynamic processes in mesoscopic scales, because it can characterize surface morphologies and structures in situ in a wide range of magnifications. In the present paper, we applied the UHV-SEM combined with micro-probe RHEED to investigate the electromigration of Ag and In film patches on clean and Au-precovered Si(1 1 1) surfaces, and found remarkable anisotropic features of diffusion, due to either surface steps or substrate surface structures.

In some previous studies, the preferential migrations of Ag or In thin film on the clean Si(1 1 1)-7×7 surface have already been reported [11,12,19,21]. Also, it has been noticed that on a vicinal Si(1 1 1) surface, the atomic steps can influence the lateral diffusion rate in the above-mentioned two systems [12–14]. Namely, for Ag/Si(1 1 1) the migration was enhanced in the direction parallel to the step edges, while no appreciable influence was noted in the direction perpendicular to the step edges. On the other hand, for In/Si(1 1 1), the migration normal to the steps was greatly reduced whereas the migration along the steps remained unchanged. In our SEM observations in the present study, we further found that: (1) The electromigration direction was determined by combination of the external applied direct-current direction and step orientation on the surface. In the case of an Si(1 1 1) surface with inclined steps with respect to the current, the electromigration direction was not exactly along the current. (2) The diffusion anisotropy depends not only on surface steps or step bands, but also on the adsorbate structures on the substrate. The substrate—structure dependences of Ag and In migrations were quite different from each other.

2. Experimental

The experiments were carried out in a UHV chamber equipped with a customized Hitachi S-4200 field-emission SEM and micro-probe RHEED apparatus, which is schematically shown in Fig. 1. The base pressure of this system was 2×10⁻⁹ Pa, while during deposition the pressure was kept below 1×10⁻⁷ Pa. Sample cleaning by direct-current heating and metal depositions can be carried out on the SEM stage. In order to enhance the surface sensitivity, the primary electron beam irradiated the sample surface with a grazing incidence (about 10° from the surface), while RHEED observations were done with an angle of incidence less than 5°. Because of grazing incidence of the primary electron beam, the SEM images shown here were foreshortened by a factor of about five in the vertical direction. The acceleration voltage of the electron beam was 30 kV. The beam diameter was about 2 nm on the sample surface. SEM observations were in situ done before, during, and after the current stressing to the sample. This system also enables scanning reflection electron microscopy, which is not used here.

The substrate bar (typical size: 15×3×0.4 mm³) was cut from a mirror-polished, nominally non-misoriented Si(1 1 1) wafer with a resistivity of 50–100Ω cm in n-type. It was cut in such a way that its longer sides were parallel to the (1 1 0) direction, which made the steps oriented in a direction normal to the current. To compare the effect of different orientation of surface steps, we also cut the substrate with its longer side parallel to the (1 1 2) direction, or several degrees off the accurate (1 1 0) and (1 1 2) directions. The substrate was mounted between two Ta electrodes, and was resistively heated to 1473 K for cleaning, followed by annealing around 1073 K by passing the current along the longer side. Then a well-ordered 7×7 surface was obtained as observed by RHEED. The direct-current direction was selected to make bunching steps on the substrate. The substrate temperature was measured with an optical pyrometer.

Ag or In was deposited through an Mo mask (with a rectangular window whose width was 150 μm) onto the center of the substrate surface at room temperature (RT), by thermal evaporation from a heated alumina-coated tungsten basket, to make a reproducible well-defined film patch. The
mask was set just in front of the sample surface with a manipulator (see Fig. 1). For the studies on Au-precovered Si(111) surfaces, prior to the deposition of Ag or In patches, Au was evaporated from another basket onto the whole substrate surface (without using the mask) at 873 K. Au deposition amount was controlled to induce different reconstructions \cite{23} \((5 \times 2, \alpha-\sqrt{3} \times \sqrt{3}, \text{and} \ \beta-\sqrt{3} \times \sqrt{3})\). The deposition rates of Ag, In, Au were estimated by separate high-temperature deposition measurements with the aid of RHEED pattern. The thicknesses of Ag (5.8 or 5.3 ML) and In (2.0 ML) of thin film patches in the present experiment were nominal ones determined through the induced reconstructions by the respective elements (\(\sqrt{3} \times \sqrt{3} \) phase with 1 ML Ag or \(\frac{1}{3}\) ML In). To drive the mass transport, a constant direct current was fed through the substrate along its longer side.

3. Results

3.1. Ag migration on Si(111)

Fig. 2 shows a step effect on Ag migration. Fig. 2(a) reproduces an SEM image of an Ag film patch in as-deposited state on a 7\(\times\)7 clean surface. Step bands (where about 40 bi-layer steps are accumulated) were arrayed along the vertical direction with about 10\(\mu\)m spacing. The image (b) was taken after feeding a direct current of 0.42 A (813 K) for 10 min from left to right. It is noted that the Ag patch spreads out in the direction normal to the surface step bands, i.e., along the direct-current direction, towards the cathode side. The thermal diffusion due to Joule heating effect towards the upside and downside seems equal. The patch area showed a \(\sqrt{3} \times \sqrt{3}\) RHEED pattern.

In contrast, from Figs. 2(c) and (d), which similarly correspond to an as-deposited Ag film patch and after current stressing (0.35 A, 813 K) for 5 min from right to left, respectively, on a 7\(\times\)7 surface with step bands inclined to the current direction, it was found that the spread-out Ag layer showed a tendency to direct to the lower left corner, although the current direction was still along the horizontal direction in this image. The electromigration direction was still generally towards the cathode side. Considering that the symmetrical centerline of the as-deposited Ag patch was off the horizontal direction in (c), we estimated that the deviation angle of electromigration was about 10\(^\circ\) off the original symmetrical centerline, but several tens of degrees off the current direction in (d). In the latter case, the apparent lateral expansion of the Ag film patch looks asymmetric between the upward and downward directions in (d). This apparent feature may be caused by a combined effect of electromigration along the current direction and migration along step band arrays inclined with respect to the current direction. Ag atoms thermally diffusing upwards will be forced to return downwards, while the atoms thermally diffusing downwards will be accelerated by the electromigration force. A similar step effect was also noted on various Au-precovered Si(111) surfaces, regardless of Au coverages and corresponding...
superstructures, although the migration speeds were different depending on the Au coverages as shown below.

In separate experiments using Si substrates with steps arrayed parallel to the current direction, it was found that the electromigration was exactly along the current direction. It should be mentioned that for Ag on the clean 7×7 surface, the anisotropic migration depending on the direction and sense of the step bands was also noted by Shidahara et al. through a photoemission electron microscopy (PEEM) study [22]. Based on these observations, it can be said that the actual electromigration direction for Ag on Si(111) is determined by both current direction and step orientation on the surface.

Figs. 3(a) and (c) are again as-deposited Ag patches on a mixed phase of 5×2-Au and \( \alpha\sqrt{3} \times \sqrt{3}\)-Au structure (Au coverage \( \theta_{Au} \sim 0.71\) ML) (abbreviated to \( (5\times2+\alpha\sqrt{3}) \) hereafter), and on a single phase of \( \beta\sqrt{3} \times \sqrt{3}\)-Au (\( \theta_{Au} \sim 1.0\) ML) at RT, respectively, (b) and (d) are
after current stressing. The patch spreads anisotropically on the \((5 \times 2 + \sqrt{3})\) substrate as on the \(7 \times 7\) substrate (Fig. 2), while the patch on the \(\beta - \sqrt{3} \times \sqrt{3}\) substrate shows no spreading even with much longer current-stressing duration. The Ag patch showed the largest spreading on the \((5 \times 2 + \sqrt{3})\) substrate, while the smallest spreading was on the \(\beta - \sqrt{3} \times \sqrt{3}\) substrate. The patches on both substrates showed \(\sqrt{3} \times \sqrt{3}\) RHEED patterns during current stressing (at elevated temperatures), while they changed into \(\sqrt{21} \times \sqrt{21}\) patterns after cooling to RT by cutting the current.

3.2. In migration on Si(1 1 1)

Fig. 4 reproduces a series of SEM images, which show the features of surface migration of an In film patch on a clean \(7 \times 7\) surface. Fig. 4(a) describes the shape and location of the In patch just after RT deposition. Figs. 4(b)–(d) show a sequence of the In patch evolution with current-stressing time, from 1 to 30 min with \(I = 0.1\) A at \(T = 630\) K. The corresponding RHEED pattern showed that the structure of the In film patch after feeding the direct current was always a \(1 \times 1\) structure [24], while the original In film in (a) did not show any ordered RHEED pattern. It is clear that at this stage with the current of 0.1 A feeding, migration of In parallel to the current direction towards the cathode side was obviously suppressed by the step bands; rather, only the transverse migration along the step bands due to thermal effect can be seen. It should be mentioned here that since the images are foreshortened by a factor of about five in the vertical direction, the observed
lateral migration along the step bands should be read about five times larger.

When the stressing current was increased to 0.3 A (763 K), as shown by Fig. 4(e), the In film patch showed a spread along the current over step bands. But it is not so remarkable compared with the Ag case in Fig. 2. The brighter region at the central part of the patch remained the 1×1 structure in RHEED, and the dark region, as indicated above, was the 7×7 surface. The middle bright region at the periphery of the patch was a $\sqrt{3} \times \sqrt{3}$ structure. However, the spread-out intermediate layer for In migration on Si(1 1 1) was reported to be a 4×1 structure in previous results on this In/Si(1 1 1) system [18,19,23]. With a longer current-stressing duration, the central part with the 1×1 structure gradually shrank (Fig. 4(f)), and finally disappeared, leaving the whole film patch with the $\sqrt{3} \times \sqrt{3}$ structure only (Fig. 4(g)). However, from some contrast outside the In patch, there existed a domain of $(7 \times 7 + \sqrt{3} \times \sqrt{3})$ mixed structure. In this way, compared with Fig. 2, the In patch behaves in a quite different way from the Ag patch on the 7×7 clean surface, although the effects of step-edge barriers on migration are similar to each other.

By increasing the current from 0.1 to 0.3 A in Fig. 4(e), the migration of In along the current direction over step bands was apparently enhanced. The migration process is generally a thermal-activation phenomenon, so that by increasing the current and the resulting substrate temperature, the migration speed will be exponentially enhanced. A possible explanation for the enhanced migration in Fig. 4(e) from a different point of view is that this may be related to a phase transformation on the surface. The In patch showed only the 1×1 RHEED pattern under 0.1 A stressing in (b)−(d), while it began to show a $\sqrt{3} \times \sqrt{3}$ pattern at the periphery of the patch under 0.3 A stressing in (e). When the substrate temperature is high enough for forming the $\sqrt{3} \times \sqrt{3}$ phase, In atom migration will be enhanced.

Fig. 5 shows a series of SEM images which describe the evolution of In film patch on a 5×2-Au surface ($\theta_{Au} \sim 0.5$ ML) during electromigration. The original patch was almost the same as that shown in Fig. 4(a). Figs. 5(a) and (b) are after current (0.1 A, 630 K) was applied for 1 and 10 min, respectively. Similar to that on the clean 7×7 substrate (Fig. 4), no apparent electromigration along the current was observed at this stage, except some transverse thermal diffusion along the step bands. When the current was increased to 0.2 A (709 K) in Fig. 5(c), it can be noted that the In patch preferentially migrated towards the cathode side, and the transverse thermal migration was overwhelmed by electromigration part.

Fig. 6 shows the evolution of the In patch on a surface of a $(5 \times 2 + z - \sqrt{3})$-Au mixed phase ($\theta_{Au} \sim 0.7$ ML). (a), (b), and (c) correspond to the SEM images after current (0.1 A, 630 K) was applied for 5, 10, and 30 min, respectively. In contrast to that on the 7×7 and 5×2-Au surfaces mentioned above, under the same conditions (current, substrate temperature, as well as current-stressing time), the In patch migrated obviously faster both towards the cathode side due to electromigration along the current and laterally along the step bands due to thermal effect.

In strong contrast to the above-described three kinds of surfaces, the migration of an In film patch on the $\beta$-$\sqrt{3} \times \sqrt{3}$-Au surface ($\theta_{Au} \sim 1$ ML) under the effect of direct current was found to show the most anisotropic feature. Fig. 7(a) shows the In patch after 0.1 A of current was applied for 1 min, showing that In atoms can easily migrate across step bands, in a direction parallel to the current. Only for 4 min stressing by current (0.1 A), the original In film patch spread about 350 μm towards the cathode, as shown in Fig. 7(b). However, the lateral expansion of the In patch normal to the current direction was suppressed.
remarkably, and with a longer current-stressing duration, the In patch clearly showed a tendency of reduction in width. Fig. 7(c) was taken at a place near the front edge of the In patch indicated in (b). Large dark spots about 0.5 μm in size show three-dimensional Au islands which had been formed by initial Au deposition, while many smaller dark spots about 50 nm in size correspond to In islands coming from the original In film patch on the left side out of this image. The
RHEED patterns taken in the spread-out In film patch on the above-mentioned Au-precovered surfaces were too complicated to be analyzed at present.

The results presented here are summarized as follows. (1) The migration anisotropy of In on Si(1 1 1) surface was influenced by both steps and Au/Si adsorbate superstructures. (2) The electromigration velocity and spread ability of an In film patch were greatly enhanced on the $\beta$-$\sqrt{3} \times \sqrt{3}$-Au surface, which is the opposite of the Ag case described in the previous subsection.

4. Discussions

It will be convenient to discuss the reason for the substrate–structure dependences of the migration behaviors of Ag and In atoms on the Au-precovered substrates from two points of view;
one is an influence on the migrations on terraces, and the other is an influence on the migration across step edges. Different Au coverages induce different surface superstructures on which Ag and In atoms will migrate differently due to different corrugations in migration potentials or due to formations of different surface alloy phases, resulting in different effective charges of migrating species and resultant different driving forces for electromigration. On the other hand, different Au coverages will make migration barriers at step edges different, inducing apparently different migration speeds over step edges.

By comparing Fig. 4 with Fig. 7, it is clear that the step-edge barrier for In migration on the 7×7 surface seems to be reduced on the β-√3 × √3-Au surface, leading to an acceleration of migration over step bands. Moreover, as will be discussed later, the β-√3 × √3-Au surface may act as an intermediate layer over which In atoms can migrate quite easily, because if not, the In patch would not spread as rapidly as observed in Fig. 7. On the other hand, by comparing Fig. 3(d) with Fig. 2 for the case of Ag migration, the main reason for the negligible migration of Ag on the β-√3 × √3-Au surface does not seem a large step-edge barrier, because no transverse diffusion on the respective terraces like in Fig. 4(b) was seen for the Ag case. The step-edge barrier for Ag on the β-√3 × √3-Au surface is similar to that on the 7×7 surface, because the anisotropic expansion of the Ag patch similar to Fig. 2(d) was also observed on the β-√3 × √3-Au substrate (Fig. 3(b)). In Fig. 3(d), the diffusions in directions both along and perpendicular to the current are negligible, which implies a reduced migration on terraces as a main reason for the negligible expansion of the patch. Thus, the β-√3 × √3-Au structure influences the migrations of In and Ag atoms in quite different ways: it acts to reduce the step-edge barrier for In migration, while it acts to reduce the migration on terraces for the Ag case.

It is instructive to compare our results with that of Kono’s group about In migration on the Si(111) surface [24]. In their experiment, the electromigration was performed using an In film patch on the Si(111)-4×1-In surface, i.e., to study the In migration on an In-precovered Si(111). The resistivity and step orientation of the sample substrate were similar to ours, but the current and substrate temperature were different. The electromigration velocity they measured at a substrate temperature of ~373 K was of the same order, ~100 μm/min, as in our observation on the β-√3 × √3-Au surface (Fig. 7). Considering the fact that In migration on the clean 7×7 surface is hindered by steps as revealed in Fig. 4 and also in a report by Yasunaga et al. [12], our results and those of Kono et al. may imply that In atoms can rapidly migrate across steps with the existence of a pre-covered intermediate layer on the whole substrate surface. Since it has been known that the 4×1-In is an intermediate layer for In atom migrating on the Si(111), we assume that the β-√3 × √3-Au also acts as an intermediate layer for In migration. From this point of view, the step-edge barrier for migration is reduced on the intermediate layer surface compared to that on the 7×7 clean surface. The diffusion on terraces is probably also enhanced on the intermediate layers (though quantitative analyses are not given here).

We discuss more about the comparison between In (Figs. 4–7) and Ag (Figs. 2 and 3) migrations in the present study and also with Cu migrations [25,26] on the same Au-precovered Si(111) surfaces. Electromigration of In is found to be enhanced on the β-√3 × √3-Au surface, while Ag and Cu atoms showed almost negligible electromigration on this surface. The 5×2-Au and (5×2 + a–√3)-Au surfaces are the substrates with lower mobility for In atoms, while these surfaces enhance the mobility for Ag and Cu atoms. In this way, In shows quite different behaviors in electromigration from Ag and Cu atoms on the Au-precovered surfaces. One of the reasons for this difference may be the surface superstructures formed in the film patches during migration. The In patch forms some complicated surface alloy structures on the Au-precovered substrates, while Ag and Cu patches always make √3 × √3 structures accompanied with v21 × v21 structures. So surface alloy phases with Au (and also Si) are different between In case and Ag/Cu cases, causing a difference in mobility and ability of expansion of the film patches. From this point of view, migration on terraces also can be a
dominant factor for determining the migration speed.

5. Conclusion

We have observed a remarkable migration anisotropy in Ag/Si(111) and In/Si(111) systems. For Ag on clean and Au-precovered Si(111) surfaces, it was found that electromigration of Ag shows anisotropy upon differently oriented step structures. The actual electromigration direction was determined both by current direction and by steps (bands) orientation on the substrate surface. However, no influence of Au/Si adsorbate structure on the migration anisotropy has been noted, meaning similar step-edge barriers for migration on all the Au-precovered and clean Si(111) surfaces. Ag showed negligible migration on the $\beta\sqrt{3} \times \sqrt{3}$-Au surface due to reduction of migration on terraces, while the $7 \times 7$ surface was the substrate for appreciable migration of Ag atoms. For In migration on the $\beta\sqrt{3} \times \sqrt{3}$-Au surface, on the other hand, the step influence on the migration observed on the $7 \times 7$ clean surface was masked, so In migrated with the highest mobility across step bands towards the cathode side. We suppose that the $\beta\sqrt{3} \times \sqrt{3}$-Au surface phase may act as an intermediate layer for In migration. The difference in migration behaviors between In and Ag on the Au-precovered Si(111) surfaces was discussed in terms of step-edge barriers and on-terrace migration. The $7 \times 7$ surface showed appreciable step-edge barriers for both Ag and In.

Acknowledgements

This work has been supported in part by Grants-in-Aid from the Ministry of Education, Science, Culture, and Sports of Japan, especially through those for Creative Basic Research (No. 09NP1201) conducted by Prof. K. Yagi of Tokyo Institute of Technology, and also for an International Joint Research (No. 11694059). We have been supported also by Core Research for Evolutional Science and Technology Corporation conducted by Prof. M. Aono of Osaka University and RIKEN.

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