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Temperature dependence of growth mode and epitaxial orientation on Au/Ni(111)

M. Hashimoto [a,*], K. Umezawa [b], T. Yasue [a], T. Koshikawa [a]

[a] Fundamental Electronics Research Institute, Osaka Electro-Communication University, 18–8 Hatsu-cho, Neyagawa, Osaka 572–8530, Japan
[b] Department of Physical Science, Osaka Prefecture University, 1–1 Gakuen-cho, Nakaku, Sakai, Osaka 599–8531, Japan

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ABSTRACT

Growth processes of Au on Ni (111) surface at various substrate temperatures between 150 °C and 400 °C were investigated with low energy electron microscopy (LEEM). Au–Ni surface alloy forms in the beginning of growth and the following de-alloying results in the formation of the Au overlayer above 0.3 ML. The growth modes after that depend on the substrate temperature. Above about 300 °C, Au grows with layer-by-layer fashion up to 2 ML and the multilayer growth follows. On the contrary, the multilayer growth takes place from the initial stage below about 300 °C. Areas with the different epitaxial orientations of Au(111) film, Au(111)$\left[11\bar{2}\right]$//Ni(111)$\left[11\bar{2}\right]$ and Au(111)$\left[\bar{1}\bar{1}2\right]$//Ni(111)$\left[11\bar{2}\right]$, were separately imaged using dark-field LEEM. But the clear correlation between the area distribution with different epitaxial orientation and surface morphology was not recognized on the terrace.

1. Introduction

During the formation of heteroepitaxial interface of bimetallic system, metallic alloy often forms in the beginning of growth. Elemental Au–Ni is immiscible in the bulk, and the lattice mismatch between Au and Ni is relatively large (15.7%). It is known, however, that the Au/Ni(110) surface alloy can form within the outermost layer of the Ni substrate in the very beginning of growth [1–3]. Then, de-alloying follows after 0.4 ML of Au deposition [4,5], and the Au monolayer forms on the substrate. The similar surface alloy formation has been also observed on Ni(111) [6,7]. Such Au–Ni surface alloy on Ni(111) attracts much interests on catalytic reactions of several gases [7–10].

Umezawa et al. have reported a temperature dependent peculiar epitaxial growth of Au on Ni(111) surface [11,12]. Au thin film grows epitaxially on Ni(111) and shows two kinds of epitaxial orientation relationship; Au(111)$\left[11\bar{2}\right]$//Ni(111)$\left[11\bar{2}\right]$ and Au(111)$\left[\bar{1}\bar{1}2\right]$//Ni(111)$\left[11\bar{2}\right]$. The former is named as 'normal mode' and the latter as 'reverse mode'. They found that area fractions of these two modes alternatively vary with the substrate temperature using low energy ion scattering technique. Later such coexistence of two orientations has been confirmed qualitatively by medium energy ion scattering study [13]. Ion scattering, however, only gives area-averaged information about the static surface, hence does not provide any insight about dynamic processes of alloying, dealloying and growth or the spatial inhomogeneity identified previously in this system.

Low energy electron microscopy (LEEM) is one of powerful tools to investigate the local information of ~10 nm of the thin film growth process on the surface dynamically [14,15]. The diffraction contrast gives us the structural information of the growing film. The rotationally symmetric structures around the surface normal such as the normal and reverse modes of Au/Ni(111), however, cannot be distinguished in the bright-field image, where the (00) beam is magnified. Whereas the dark-field imaging with the integer-order spots is effective in such cases. For example, the Ru(0001) surface exhibited contrast between terraces separated by an atomic step in the integer-order dark-field image because the atomic arrangement of the topmost layer is rotated by 180° on the neighbor terraces [16].

In the present study, we have studied the growth behavior of Au/Ni(111) with LEEM. In the following, dark-field imaging will be shown in conjunction with bright-field imaging. These observations provide new insight about the temperature dependent growth mode, relation between surface morphology and epitaxial orientation.

2. Experimental

The sample used was a mirror polished Ni(111). Ni(111) surface was initially cleaned by many cycles of Ar^+ ion sputtering, whose energy was 2 keV, and heating up to about 650 °C in a separate chamber from the LEEM apparatus. The clean surface was checked by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). After introducing into the LEEM system, several cycles of sputtering and annealing were repeated before deposition of Au. Finally the clean Ni(111) surface was confirmed with LEED and LEEM. Au was evaporated from a Mo crucible which was heated by electron bombardment. Deposition rate was about 0.1 ML/min, which was estimated by

* Corresponding author. Tel.: +81 728241131.
E-mail address: h-michi@isc.osakac.ac.jp (M. Hashimoto).

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the completion of the first monolayer at high temperature with LEEM (see Fig. 1). Substrate temperature was estimated using a thermocouple attached to the sample cartridge. The error of the estimated temperature would be about 50 °C. The growth process of Au/Ni(111) was observed using a bright-field LEEM and the structure of the overlayer was investigated by LEED. The normal and reverse mode cannot be distinguished by the bright-field LEEM, so that the integer-spot dark-filed LEEM was employed to determine the area ratio between two modes. LEEM equipped with a high brightness and highly spin polarized electron source [17–19] was employed in the present study, but an unpolarized electron beam was used in order to exclude unexpected magnetic contribution to the LEEM contrast because the substrate is a ferromagnetic material.

3. Results and discussion

3.1. High temperature growth mode

The growth processes of Au/Ni(111) observed in the present study are roughly classified into two modes. High temperature growth mode takes place above about 300 °C. Fig. 1 shows bright-field LEEM images during deposition of Au on Ni(111) surface at about 400 °C, and a corresponding growth process is schematically depicted in Fig. 2. Fig. 1(a) is a LEEM image of a Ni (111) clean surface. Monoatomic steps can be seen in the middle of the image, while step bunches are recognized at the upper and lower sides of the image. No remarkable change of the contrast in LEEM image was observed in the very beginning of deposition below 0.3 ML. It is well established that the Au–Ni surface alloy forms in the early stage of growth on Ni(111) surface [6,7] as well as on Ni(110) surface [1–3]. The ion scattering technique revealed that the surface alloy phase has formed within 0.4 ML on Ni(111) surface [12]. Therefore, it is considered that impinged Au atoms form a uniformly distributed surface Au–Ni alloy as shown in Fig. 2(b) and it could not be detected in the LEEM observation. Beyond 0.3 ML, the decoration of steps starts as seen in Fig. 1(b). Umezawa et al. have observed the coexistence of the Au–Ni surface alloy and Au overlayer in between 0.4 ML and 1 ML [12]. Similarly, it has been shown that de-alloying occurs above 0.4 ML also in Au/Ni(110) [4,5]. It is considered that the decoration of steps is due to the formation of the Au overlayer at step edges which is resulted in de-alloying as illustrated in Fig. 2(c). Next, as seen in Fig. 1(c), the two-dimensional layer extends in a certain specific direction from the step edge. The Au overlayer spreads over the surface and coalesces with each other as seen in Fig. 1(d), and finally the surface is fully covered by the Au monolayer in Figs. 1(e) and 2(d). The coverage here is defined as being 1 ML. The Au overlayer shows 9 × 9 reconstruction (see LEED patterns shown in Fig. 5). The 9 × 9 Moiré structure has been observed with STM, and the structure model was proposed [20]. The de-alloying leaves Ni vacancies under of the Au layer, and Ni vacancies induce the further shift of Ni atoms from fcc to hcp sites. With further deposition of Au, the second layer starts to form with elongated feature as shown in Fig. 1(f). Although the elongated feature in Fig. 1(f) is similar to that in Fig. 1(d), the growth behavior is completely different. As seen in Fig. 1(c) and (d) the elongated domains extend along some direction and form the continuous first layer shown in Fig. 1(e). The domain boundaries, however, might remain at this moment. The subsequent Au nucleation preferentially occurs at the domain boundaries and the elongated feature appears again as shown in Fig. 1(f) in the early stage of the second layer formation. The further Au deposition destroys the elongated feature and the nucleation and growth on the terrace follows in Fig. 1(g). The second layer continues to form and the whole surface is covered with the second layer as shown in Fig. 1(i). At the step bunch, completion of the second layer is earlier than that on the terrace, so that the nucleation of the three-dimensional islands, which are observed as the bright dots in Fig. 1(i) and (j), starts before the completion of the second layer on the terrace. After the completion of the second layer, multilayer growth takes place on the terrace. In Fig. 1(j), a slight difference of the contrast in the layer on the terrace can be seen. This is an evidence of the multilayer growth, and the contrast arises due to the quantum size effect [21]. Therefore the layer-by-layer growth takes place up to 2 ML and the island growth and/or the multilayer growth follows at this substrate temperature regime.

3.2. Low temperature growth mode

The growth behavior in the low temperature mode takes place below about 300 °C. Fig. 3 shows a series of bright-field LEEM images during Au deposition on Ni (111) surface at about 250 °C. The initial Ni (111) surface has no step bunch as shown in Fig. 3(a). With deposition of Au, not only the step decoration but also the condensation on terraces takes place in the low temperature regime as seen in Fig. 3(b). In contrast to the high temperature growth mode, the Au–Ni surface alloy does not uniformly form on the surface due to the shorter diffusion length of impinged Au atoms. The dark patches on the terrace grows with Au deposition, however the darker contrast appears in the center of the patches at about 0.3 ML as shown by the arrow in Fig. 3(c). Such darker area is considered to be the Au overlayer resulted in de-alloying. Note that the contrast of the de-alloying area seen here is different from that in Fig. 1 because of the different imaging condition. The Au overlayer extends by the subsequent deposition, but the completion of the monolayer does not occur as seen in Fig. 3(d)–(f). Instead several gray levels are recognized in the

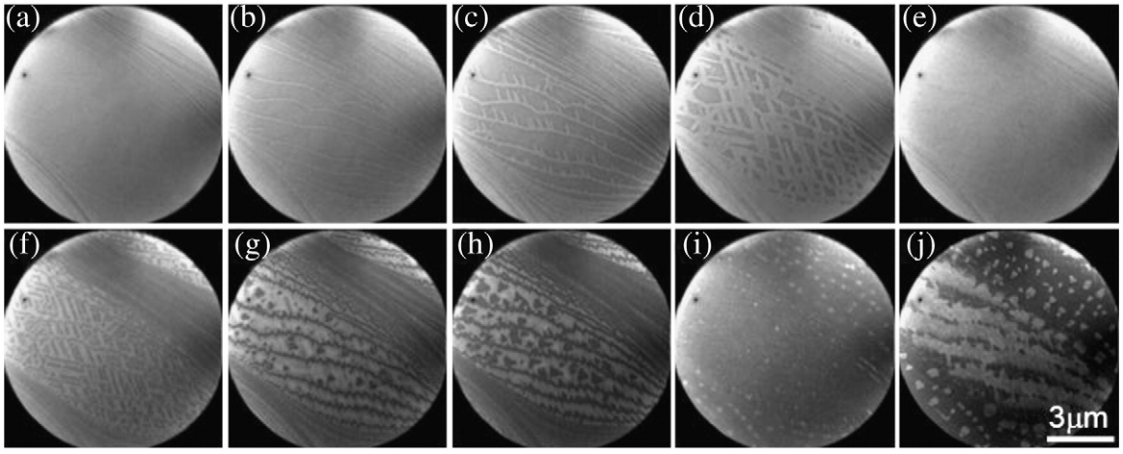

Fig. 1. Bright-field LEEM images during the growth process of Au/Ni(111) at about 400 °C. The field-of-view is 10 μm, and the images are taken at the electron energy of 1 eV. (a) a clean Ni(111), (b) 0.31 ML, (c) 0.41 ML, (d) 0.63 ML, (e) 1.00 ML, (f) 1.24 ML, (g) 1.49 ML, (h) 1.66 ML, (i) 2.25 ML and (j) 3.44 ML.