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Surfactant-Mediated Epitaxial Growth of Fe/Fe(100) and Cr/Fe(100)

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The effects of several surfactants (Pb, Bi, and Ag) on the homoepitaxial growth of Fe(100) have been studied and compared. Our measurements clearly revealed that Pb and Bi were effective surfactants for enhancing layer-by-layer (LBL) growth in the Fe(100) homoepitaxy. Ag had the same effect, but it was less efficient due to the weak surface segregation of Ag. Using a surfactant Bi, we investigated the surfactant effect on the heteroepitaxial growth of Cr on Fe(100). It was found that a suitable amount of Bi enhanced the LBL growth of Cr on the Fe(100) surface. The surfactant effect of Bi on the heteroepitaxial growth of Fe/Cr(100) multilayers on the Fe(100) surface was also investigated. Predeposition of a small amount of Bi (0.08 ML) enhanced the LBL growth of the Fe/Cr(100) multilayer. The interface structures of the Fe/Cr multilayer with Bi were sharper as compared to the multilayer without Bi.

Key words: Crystal growth, Thin film, RHEED, Surface morphology, Surfactant

1. INTRODUCTION

Recently, it has been demonstrated that the use of surfactants can alter the film morphology during epitaxial growth for semiconductors [1] as well as metals [2]. The implementation of surfactant-mediated epitaxy, where the surfactant atoms are pre-deposited onto a substrate surface prior to growth, can control the surface energy and growth kinetics. Therefore, surfactant epitaxy is a useful method for changing the thin film growth mode from three-dimensional (3D) island formation to layer-by-layer (LBL) growth. A study by van der Vegt *et al.* reported considerable surfactant effects in the growth of metal on metal [3]. In our previous studies, we used Bi as a surfactant and found experimentally that it induced the LBL or step-flow growth of metal on metal surface [4–9].

The surfactant atoms are required to float on the surface in order to sustain the effect of changes in the growth surface morphology. Surfactants, therefore, are required to satisfy some conditions necessary for surface segregation. Mae *et al.* investigated the segregation of the surfactant atoms on the surface by the computer simulations using the modified embedded atom method [10]. The calculations indicated that the most important characteristic of the surfactant atoms should be an atomic radius greater than that of the film and substrate atoms. Furthermore, it is favorable for the surfactant to have lesser cohesive energy or surface energy than that of the film and substrate elements and it should be immiscible with these elements. In our present study, Pb, Bi, and Ag have been selected as the surfactants in the growth of Fe and Cr on Fe(100). Table I lists the atomic (metallic) radii and surface energies of these surfactant elements, Fe, and Cr [11-13]. As shown in Table I, all the studied surfactants have considerably larger atomic radii and lower surface energies than those of Fe and Cr. From the phase diagrams, it is confirmed that these surfactant elements do not alloy with Fe and Cr at less than 200 °C. Therefore, Pb, Bi, and Ag are good surfactants for the growth of Fe and Cr on the Fe surfaces.

Table I. Metallic radii and surface energies of Fe, Cr, Ag, Pb, and Bi [11–13].

Element	Fe	Cr	Ag	Pb	Bi
Metallic radius (Å)	1.26	1.25	1.44	1.70	1.78
Surface energy (J/m^2)	2.22	2.30	1.25	0.60	0.49

This study reports the influences of the surfactants on the homo and hetero-epitaxial growth of Fe and Cr on the Fe(100)-*c*(2×2)O reconstruction .This research also observes the surfactant effect on the heteroepitaxial growth of Fe/Cr(100) multilayers on Fe(100) surface.

2. EXPERIMENTAL PROCEDURE

Molecular beam epitaxy experiments were performed in this study. Fe(100) buffer layers were fabricated by evaporating Fe on MgO(100) single crystals. Substrates of the MgO(100) single crystal were cleaned by heating at 850 °C for 10 min. An Fe buffer layer with a thickness of 100 Å was deposited on the substrate at a rate of 0.04–0.06 Å/s, and the growth temperature was 200 °C. The buffer layers were then annealed at 850 °C for 30 min to obtain a flat Fe(100) surface. Half-order streaks were observed between the first streaks in the reflection high-energy electron diffraction (RHEED) patterns with respect to the Fe[011] direction [5]. However, such half-order streaks were not observed in the RHEED patterns with respect to the Fe[010] direction. In previous study, Bertacco *et al.* used low-energy electron diffraction and X-ray photoemission to report that annealing promotes the oxygen surface segregation revealing a *c*(2×2) reconstruction even in films with thicknesses of the order of several hundred Å [14]. The surface structure, therefore, is considered to be an Fe(100)-*c*(2×2)O reconstruction surface. This structure gradually disappears with the deposition of adatoms. The Fe and Cr layers, and surfactants were evaporated on the Fe buffer layer at deposition rates of 0.09~0.11 Å/s and 0.01~0.02 Å/s, respectively. The thickness of the surfactant layer was varied within 1.0 ML (ML: monolayer). The deposition temperature was maintained at 100 °C during the preparation of the deposited layers. [Fe(20 Å)/Cr(10 Å)]$_n$ multilayers were fabricated onto the Fe(100) buffer layers at 100 °C. The repetition number (n) of each set of Fe and Cr layers was 6~15.

The RHEED intensity measurements were performed during the deposition at 100 °C. The surface morphology after deposition was also measured using atomic force microscopy (AFM). Auger electron spectroscopy (AES) measurements were used to determine the composition of the film surfaces. The periodic compositional modulations of the Fe /Cr multilayers were analyzed by grazing incidence X-ray reflectivity (XRR) measurements. The magnetic properties of the multilayers were investigated by means of a vibrating sample magnetometer (VSM). The resistivities were then measured by four-lead magnetoresistance (MR) measurements. Current and magnetic fields were applied parallel to the film plane. All measurements and analyses except the RHEED measurement were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1 *Surfactant-mediated homoepitaxial growth of Fe on the Fe(100)-c(2x2)O reconstruction surface*

The thickness of the surfactant layer deposited on the Fe surface was varied before subsequent Fe growth. For the Fe growth without a surfactant on an ordered Fe(100)-*c*(2x2)O surface at 100 °C, the RHEED intensity decays almost monotonically with weak oscillations [15]. This implies that the growth mode of Fe is not an ideal LBL growth.

When Fe is deposited on Fe(100)-*c*(2x2)O covered with the surfactants (Pb, Bi, and Ag), the number of RHEED intensity oscillations increases (details are shown in Ref. [15]). This implies that these surfactants enhance the LBL growth. Table II summarizes the results of temporal evolution of the RHEED specular intensity as a function of the amount of the surfactants deposited on the Fe(100)-*c*(2x2)O surface during the homoepitaxial growth of Fe at 100 °C. These results show that there exists a suitable amount of the surfactant layer that enhances the LBL growth of the Fe(100) film at 100 °C. On the basis of the RHEED results, long-lasting layered growths were identified for predeposited layers of 0.08 ML of Pb, 0.08 ML of Bi, and 0.16 ML of Ag. On the contrary, for the cases of Fe growth with 0.33 ML and 0.5 ML of Ag, the number of RHEED intensity oscillations decreases. No oscillation is observed for the growth with 1.0 ML of Ag. In this case, the RHEED intensity decays monotonically without oscillations. These results imply that 0.33 ML and 1.0 ML of Ag induce a 3D island growth, thereby changing the growth mode.

The AFM images of the surface after deposition of Fe on the Fe(100)-*c*(2x2)O surface are observed. Figure 1 shows the AFM surface topographies of Fe films (a) without the surfactant layer, (b) with 0.08 ML of Pb, (c) 0.08 ML of Bi, and (d) 0.16 ML of Ag surfactant layer. The film surface roughness was evaluated using the rms roughness method. The rms roughnesses of these surfaces measured over an area of 200 × 200 nm^2 are (a) 0.31 nm, (b) 0.17 nm, (c) 0.09 nm, and (d) 0.25 nm, respectively. The rms analysis revealed that the surface roughness decreased with a suitable amount of surfactants. The roughness is smoother in (b) and (c) than that in (a), although the films in (b) and (c) are thicker than that in (a). By comparing the AFM results and the observations of RHEED intensity evolution results (Table II), it can be observed that Pb and Bi are relatively more effective surfactants for enhancing the layer-by-layer growth of Fe(100) homoepitaxy. Ag, on the other hand, has a surfactant effect less efficient than those of Pb and Bi.

Table II. The number of RHEED intensity oscillations of the surfactants mediated epitaxial growth of Fe on the Fe(100)-*c*(2×2)O surface at 100 °C [15]. The number of RHEED intensity oscillations of the Fe homoepitaxial growth without the surfactant is about 10 times. The hyphen (–) means experimental conditions that we have never tried.

Deposition amount (ML)	Pb	Bi	Ag
0.04	–	10 ~ 20	–
0.08	20 ~ 30	30 ~ 40	10 ~ 15
0.16	10 ~ 20	20 ~ 30	15 ~ 20
0.33	10 ~ 20	20 ~ 30	5 ~ 10
0.50	10 ~ 20	10 ~ 20	0 ~ 5
1.00	10 ~ 20	10 ~ 20	0

The Auger intensities at the top of the surface were monitored to confirm the surface segregation of surfactant atoms. Figure 2 shows the surface Auger spectra for the 1.0 ML of (a) Pb, (b) Bi, and (c) Ag surfactant-mediated growth after the deposition of Fe on Fe(100)-*c*(2x2)O at 100 °C. The thickness of the deposited Fe film is 50 Å. In Figs. 2(a) and (b), the Pb$_{\mathrm{NVV}}$ peak (a) and the Bi$_{\mathrm{NVV}}$ peak (b) are located at approximately 94 eV and 100 eV, respectively. This indicates that the Pb and Bi surfactant atoms float to the top of the surface. Taking into account that the escape depth of an Auger electron from Pb and Bi atoms is about 5 Å [16], it can be concluded that a large amount of these Pb and Bi atoms was present near the top of the surface after Fe deposition. On the contrary, in Fig. 2(c), the Ag$_{\mathrm{MNN}}$ peaks are invisible. This result indicates that

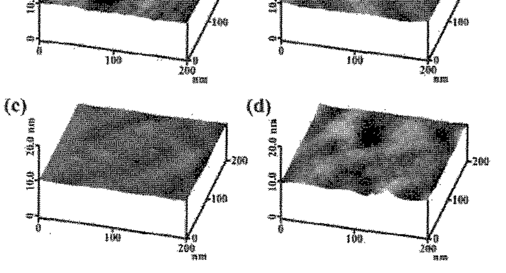

Fig.1 AFM images of the surface after deposition of Fe at 100 °C (a) without a surfactant, (b) with 0.08 ML of Pb, (c) with 0.08 ML of Bi, and (d) 0.16 ML of Ag. The thicknesses of the deposited Fe film are 50 Å (a, d) and 70 Å (b, c).

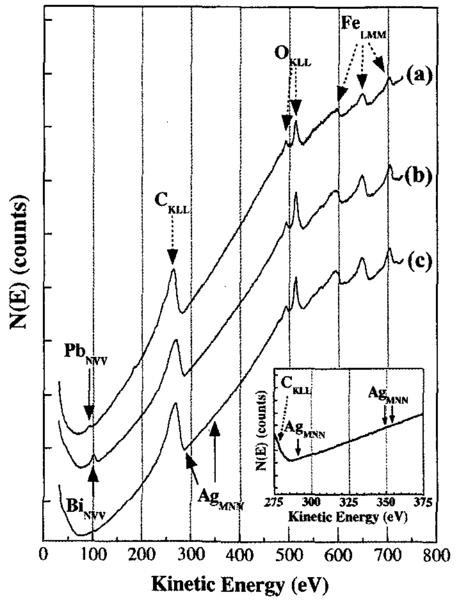

Fig.2 Auger spectrum of surfaces after deposition in 1.0 ML of (a) Pb, (b) Bi, and (c) Ag surfactant-mediated Fe(100) homoepitaxial growth at 100 °C. The thickness of the deposited Fe films is 50 Å. The inset in Fig.2 shows an enlarged area of 275–375 eV in (c). The Ag_{MNN} peaks are invisible.

Ag atoms did not effectively segregate to the surface. This is because the differences in both the atomic radius and surface energy between Pb or Bi and Fe are greater than those between Ag and Fe (see Table 1). This weak surface segregation during the growth explains the weak surfactant effect of Ag on the homoepitaxial growth of Fe(100). The C_{KLL} and O_{KLL} peaks are also clearly seen in Fig. 2. Because these AES results are not *in situ* observation data, we assume that impurities were adsorbed to the surface mainly after the deposition experiments. In fact, in the case of Fe growth without the surfactant atoms, C and O peaks were also observed in the surface AES spectrum (not shown). However, the differences in the growth behavior between surfactant mediated growth and normal growth are significant. Therefore, we speculate that these impurities do not have a considerable influence on the growth process.

3.2 *Surfactant-mediated heteroepitaxial growth of Cr on the Fe(100)-c(2x2)O reconstruction surface*

In this research, Bi was used as a surfactant in the heteroepitaxial growth of Cr on Fe(100)-*c*(2x2)O. The thickness of the surfactant of Bi layer deposited on the Fe(100) surface was varied before subsequent Cr growth. Table III summarizes the results of temporal evolution of the RHEED specular intensity as a function of the amount of Bi deposited on the Fe(100)-*c*(2x2)O surface during the heteroepitaxial growth of Cr on Fe at 100 °C, and the rms roughnesses of these surfaces after the deposition of Cr on the surface measured over an area of 200 x 200 nm^2 by using AFM. For the Cr growth without a surfactant, the RHEED intensity decays almost monotonically with weak oscillations [6]. This implies that the growth mode of Cr is not an ideal LBL growth.

When Cr is deposited on Fe(100)-*c*(2x2)O covered with the Bi surfactant, the number of RHEED intensity oscillations increases (details are shown in Ref. [6]). This implies that the Bi surfactant enhances the LBL growth. Table III shows that there exists a suitable amount of the surfactant layer that enhances the LBL growth of Cr on Fe(100) at 100 °C. On the basis of the RHEED results, long-lasting RHEED oscillations with a large amplitude were observed for predeposited layers of 0.08 ~ 0.33ML of Bi. On the contrary, for the case of the Cr growth with 1.0 ML of Bi, the RHEED intensity decays monotonically with no oscillation. This implies that 1.0 ML of Bi induces 3D island growth, and this amount of Bi changes the growth mode from layered growth to 3D island growth. As shown in Table III, the rms analysis revealed that the surface roughness decreased with a suitable amount of surfactants.

Table III. The number of RHEED intensity oscillations of the Bi surfactant mediated epitaxial growth of Cr on the Fe(100)-*c*(2x2)O surface at 100 °C and the rms roughness of surface after the deposition of 50-Å-thick Cr [6]. The hyphen (-) means experimental conditions that we have never tried.

Deposition amount (ML)	RHEED (Times)	rms (nm)
Without Bi	15 ~ 20	0.23
0.08	25 ~ 30	0.15
0.33	25 ~ 30	0.14
0.50	15 ~ 20	–
1.00	0	0.27

3.3 *The mechanism of surfactant-mediated epitaxy*

Diffusion and nucleation are the essential physical processes that determine the growth mode. In particular, the relative efficiency of the intralayer and interlayer diffusions affects the growth mode. If step crossing (i.e., interlayer diffusion) is considerably slower than surface diffusion (i.e., intralayer diffusion), a 3D growth will occur. An efficient interlayer diffusion is, therefore, necessary for a LBL growth. We discuss a mechanism of surfactant from the viewpoint of interlayer diffusion.

For adatom diffusion, there is an additional energy barrier at the step edge E_a, which is defined as the diffusion energy barrier at the descending step edges E_b minus the surface diffusion energy barrier E_d [17,18]. Therefore, a reduction in E_a will facilitate an easy descent of adatoms on the islands toward lower levels, resulting in an enhanced interlayer diffusion. Recently, it has been reported that the surfactant lowers E_a by increasing E_d, which also leads to a high nucleation density [19]. They also showed that E_d increases linearly with the surfactant coverage for the homoepitaxial growth. This behavior can be applied to our systems. With an increase in the surfactant deposition quantity, the mobility of the Fe and Cr adatoms on the Fe surface is reduced, leading to a reduced E_a caused by an increase in E_d. If E_d is, however, enhanced by a large amount of surfactant, the mobility of the adatoms will decrease markedly. This is assumed to induce a negative effect on the LBL growth. There exists, therefore, a suitable amount of surfactant layer that enhances a smoother LBL growth (shown in Tables II and III). As discussed above, an increase in E_d by surfactant deposition is proposed to be important in the LBL growth.

3.4 *Surfactant-mediated heteroepitaxial growth of Fe/Cr(100) multilayers*

Fe/Cr(100) multilayers were grown onto the

Fe(100)-*c*(2x2)O surface with and without a Bi surfactant layer. Based on the above results, 0.08 ML of Bi was deposited only one time on the Fe buffer layer at 100 °C. In case of the Fe/Cr multilayer growth without Bi, RHEED intensity oscillations were observed for the first stage (details are shown in Ref. [7]). However, after the first bilayer growth stage, the RHEED intensity oscillations decayed, and no oscillations were observed for the second growth period of the Cr layer. On the contrary, in the case of Fe/Cr growth on the Fe buffer layer covered with a 0.08-ML-thick Bi layer, the RHEED intensity oscillations with a large amplitude were clearly observed until the end of the second Fe layer growth stage. Therefore, it could be concluded that the addition of the Bi layer increased the LBL growth of the Fe/Cr(100) multilayer on the Fe(100) surface.

In order to examine the effect of Bi on the interface structure in the Fe/Cr multilayers in detail, XRR measurements were carried out. The total number of bilayers in the [Fe(20 Å)/Cr(10 Å)] multilayers was set to six. From a detailed fitting analysis, the rms value of the interface roughness of the Fe/Cr multilayer with Bi (0.58 ± 0.20 nm) was smaller than that of the Fe/Cr multilayer without Bi (0.65 ± 0.27 nm). Therefore, we concluded that the Fe/Cr multilayers prepared by Bi surfactant epitaxy had relatively flat interfaces.

In order to investigate the magnetic properties, [Fe(20 Å)/Cr(10 Å)]$_{15}$ multilayers were fabricated onto the Fe(100) buffer layers with and without a Bi surfactant layer. Table IV summarizes the results of the antiferromagnetic (AF) coupling and MR ratios of the multilayers. As shown in Table IV, the AF coupling ratio of the multilayer with predeposition of 0.08 ML Bi is larger than that of the multilayer without Bi. Therefore, the MR ratio also is increased by using a small amount of Bi. From the results of the RHEED and XRR measurements, the Fe/Cr multilayer with a Bi layer might have more sharp interfaces as compared to the multilayer without a Bi layer. Therefore, the decrease in microstructural defects in the Fe/Cr multilayers with the Bi layer increases the AF and MR ratios.

4. SUMMARY

The RHEED results proved that the initial deposition of the submonolayer of surfactants (Pb, Bi Ag) onto the Fe(100)-*c*(2x2)O reconstruction surface prior to the deposition of Fe enhanced the LBL growth process. The results of the AFM observations indicated that the rms surface roughness of Fe films mediated by Pb and Bi surfactants was considerably less than that of Fe films mediated by Ag surfactant. In addition, The AES results indicated that Ag did not effectively segregate at the surface. We used Bi as a surfactant and found that a suitable amount of Bi (0.08 ~ 0.33ML) enhanced the LBL growth of Cr on the Fe(100) surface. Predeposition of a small amount of Bi (0.08 ML) enhanced the LBL growth of the Fe/Cr(100) multilayer on the Fe(100) surface. The interface structures of the Fe/Cr multilayer with Bi were sharper as compared to the multilayer without Bi. The magnetic properties between Bi surfactant-mediated multilayer and normal one were also investigated. The MR ratio of the multilayer was increased by using the surfactant Bi.

Table IV. The antiferromagnetic (AF) coupling and the MR ratio of a [Fe(20 Å)/Cr(10 Å)]$_{15}$ multilayers with and without a 0.08 ML thick of Bi layer measured at room temperature.

Multilayer type	Without Bi	With a 0.08 ML of Bi
AF coupling ratio (%)	72.3	94.8
MR ratio (%)	8.4	11.0

5. ACKNOWLEDDGMENT

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