Surface Structures and Growth Modes of Nd Deposited on Mo(110) Surface

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Abstract

The surface structures of Nd deposited on Mo(110) surface have been investigated by RHEED. At 1 ML deposition, the c(5×3) structure appeared as the first layer of Nd which coincides with the atomic arrangement of Mo(110) surface, forming a coincident site lattice expressed as $\begin{pmatrix} 4 & 3 \\ -1 & 3 \end{pmatrix}$. At the specimen with deposition thickness more than 1.5 ML, the Nd(0001) layer is formed on the first layer of the c(5×3) structure. Using hcp expression, the epitaxial orientation relationship is (0001)Nd//(110)Mo, $[2\bar{1}\bar{1}0]$Nd//[001]Mo. This corresponds to the representative orientation relationship at the fcc(111)/bcc(110) interface, commonly called as Nishiyama-Wassermann orientation relationship. Irrelevant to the film thickness, (11×2) structure and one-dimensional periodic structure appeared at higher temperatures. The growth modes of Nd on Mo(110) surface are the Frank-van der Merwe growth mode at room temperature and the Stranski-Krastanov growth mode at higher temperatures.

1. Introduction

Several investigations on the surface structures of rare earth metals deposited on Mo(110) or W(110) surface have been carried out up to date [1-3]. In such deposition cases, various surface structures of the two-dimensional layers appear. However, most of the investi-gations are limited to room temperature condensation, and the detailed investigations on the change of surface structures for the substrate temperature are very rare. Recently, we have studied on the Ce/Mo(110) deposition system in wide temperature region using RHEED [4-6]. On the study of Nd on Mo surface LEED study about Mo(112) surface has been done by Zadorozhnyi et al [7]. In the present paper, we report the experimental results of RHEED observation of the surface structures of Nd on the Mo(110) surface with changing deposition thicknesses and substrate temperatures.

2. Experiments

All experiments were carried out in an ultra-high vacuum chamber. The base pressure was 1.0×10^{-10} Torr. The single crystal of Mo, grown by the floating zone method, was cut into the slice with the (110) plane. The deviation of the orientation is within 0.1°. The size of the substrate was 5×3×0.3mm. The cleaning procedure of the substrate was as follows. The electrolytic polishing with a solution of 97% H_2SO_4 + 3% H_2O was done until the Mo slice had a mirror surface. After the substrate was mounted on Mo ribbon heater, it was introduced in the UHV chamber. After the vacuum of the chamber attained 10^{-10} Torr range, the substrate was annealed at 600℃ in oxygen atmosphere of 1.0×10^{-6} Torr to form Mo oxide. After the vacuum attained 10^{-10} Torr range, flashing was done at 1500℃ to obtain 1×1 structure of Mo(110) surface with very low background by RHEED observation. By pre-heating the Nd with electron bombardment, the impurities in the deposition source were avoided. The deposition rate was about 2 Å/min. Nd was deposited on Mo (110) substrate with various film thicknesses and substrate temperatures. This experiment was done under two different methods. One is the deposition at room temperature followed by annealing the specimens at various temperatures. After annealing at each temperature the substrate was cooled down to room temperature to observe the RHEED pattern. The other is the depositing method during annealing of the specimen. The deposition rate and the thickness of the films were monitored using a quartz oscillator. For the specimen with ultra thin film of Nd deposited with both methods, the RHEED was used to observe the surface structures. The incident electron beam was parallel to the crystallographic 6 orientations of the Mo crystal, which is $[\bar{1}10]$, $[\bar{3}31]$, $[\bar{1}11]$, $[\bar{1}12]$, $[\bar{1}13]$ and [001] orientation, by rotating the crystal around [110] axis. The acceleration voltage was 20 kV. In this paper, the amount of Nd depositant is represented by coverage θ. The amount of Nd at θ=1 ML correspond to the thickness of 2.97 Å .

3. Results and discussion

Fig.1 shows a [1̄10]Mo RHEED pattern of the specimen deposited with Nd of 1.5 ML at room temperature and annealed at 800℃. This structure was observed in the thickness range from 1 ML to 1.5 ML thickness and in temperature range from room temperature to 850℃. In Fig.1, 1/5th order diffraction streaks by a_{Nd} was observed between 00 and 21̄ reflections of Mo. L_{01} and L_{02} Laue zones were observed between 0th and 1st Laue zones. The intensity of the streak marked as a_{Nd} is strong compared with other streaks of 0th Laue zone. From the RHEED pattern the reciprocal lattice was drawn, as shown in Fig.2. Squares and filled circles correspond to the positions of Mo and Nd reflection, respectively. All other reflections drawn by crossed marks are due to double diffraction. The unit mesh drawn by the dotted paralle-logram is that of Mo(110) surface. The unit vectors of Mo in reciprocal space is a_1^* and a_2^*. The angle between them is 54.7° . The parallelogram of solid line shows the unit mesh of Nd, in which the unit vectors are b_1^* and b_2^*, and the angle between them is 59.5° . Fig.3 shows a real lattice deduced from the reciprocal lattice. The unit vectors of Mo are a_1 and a_2, and the angle between them is 125.3° . The unit vectors of Nd are b_1 and b_2, and the angle is 120.5° . This structure is close to a monolayer of hexagonal structure of Nd(0001) plane, but slightly deformed one in which the atomic distance in the [21̄1̄0] orientation is elongated by 7.5% and in the [011̄0] orientation 5.3%. Using hcp expression, the epitaxial relationship is (0001) Nd // (110) Mo, [21̄1̄0] Nd // [001] Mo. This structure can be expressed as c(5×3) using Wood's representation. And this structure also forms a

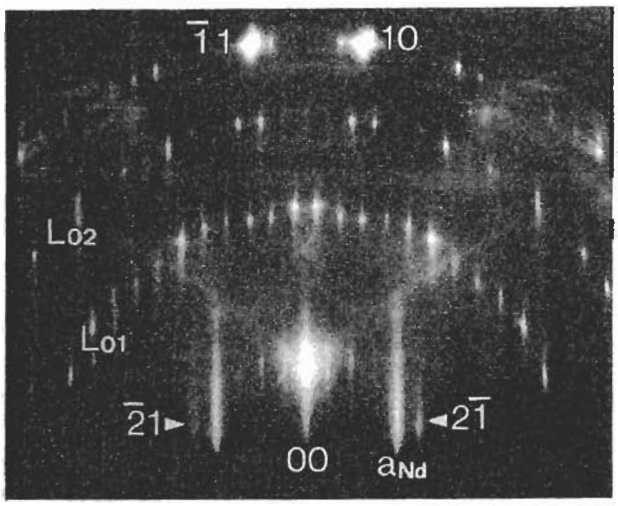

Fig.1 RHEED pattern of Mo(110) surface deposited with Nd of 1.5 ML at room temperature and annealed at 800℃. The incident electron beam is parallel to the [1̄10]Mo orientation. Notations 00 and 21̄ correspond to the fundamental reflection from Mo substrate. The notation a_{Nd} corresponds to that of Nd.

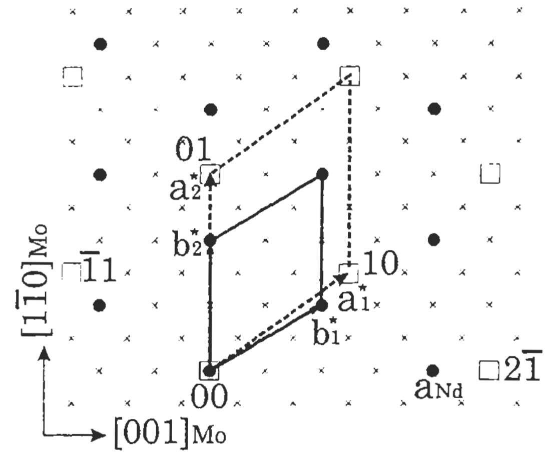

Fig.2 The reciprocal lattice obtained from the RHEED pattern shown in Fig.1. Squares and filled circles indicate reciprocal rods of Mo and those of c(5×3) structure of Nd, respectively. Crosses show double diffraction.

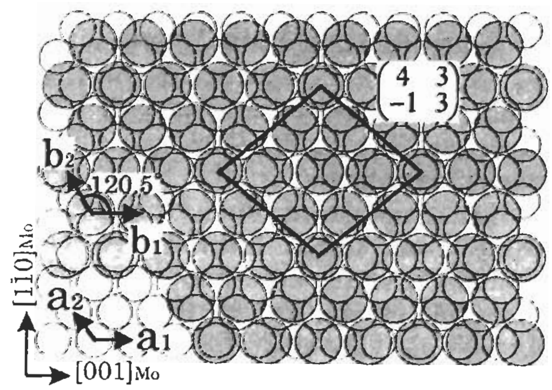

Fig.3 Real lattice model of the c(5×3) structure of Nd on the Mo(110) surface. Open circles and hatched circles indicate substrate atoms and adsorbed atoms, respectively. All atoms are drawn in correct relative sizes. The unit mesh of the coincident site lattice is shown by the large parallelogram.

coincident site lattice with the atomic arrangement of Mo(110) surface, and it can be expressed as $\begin{pmatrix} 4 & 3 \\ -1 & 3 \end{pmatrix}$. Every fifth of Mo atomic row along the [110] orientation coincides with every fourth of that of Nd. Every third of Mo atomic row along the [001] orientation coincides with every second of Nd row. Usually, the coincident site lattice means the long range coherent structure at the interface of two bulk crystals. However, in this case, coincident site lattice is realized at the interface of 1ML of Nd on the substrate.

As the substrate temperature increases, the surface structure changes to (11×2) structure at 1000℃ via complex structure. The RHEED pattern of the (11×2) structure is shown in Fig.4 whose incident electron beam is parallel to the [$\bar{1}$10]Mo orientation. The 1/11 order reflections appear between 00 and 2$\bar{1}$ Mo main reflections in 0th Laue zone and also between $\bar{1}$1 and 10 reflections in 1st Laue zone. From these observations, the real lattice is shown in Fig.5. This structure can be expressed as the (11×2) structure using Wood's notation and $\begin{pmatrix} 5 & -1 \\ 1 & 2 \end{pmatrix}$ structure as matrix notation. The appearance of this structure is caused by the evaporation of Nd on the substrate by high temperature annealing.

At higher temperature, the RHEED pattern changes to long streak pattern with equi-distance which varies continuously with the rotation of the crystal around the [110] axis.

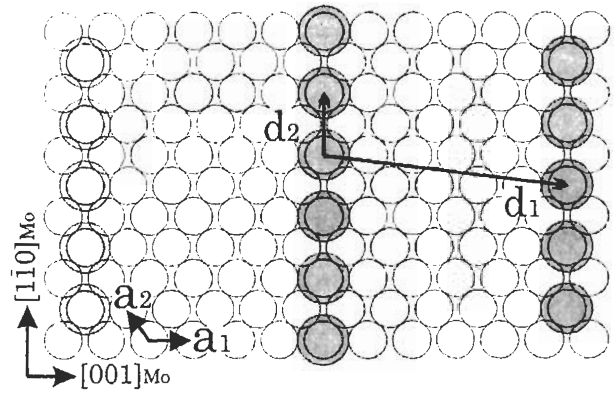

Fig.5 Real lattice model of the (11×2) structure of Nd on the Mo(110) surface. Open circles and dark circles indicate substrate atoms and adsorbed atoms, respectively. The unit mesh of this structure is represented by d_1 and d_2 vectors. All atoms are drawn in correct relative sizes.

This means the existence of reciprocal sheets in reciprocal space and from this fact it is found that one-dimensional periodic structure is formed. The Nd atoms arrange with the same atomic distance in the [001] orientation of Mo but the Nd atomic rows of this orientation have no correlation between them. Finally, the Mo clean surface appears at the temperature more than 1250℃.

Fig.6 shows a RHEED pattern of the Mo(110) surface deposited with Nd of 2.5ML at room temperature followed by annealing at

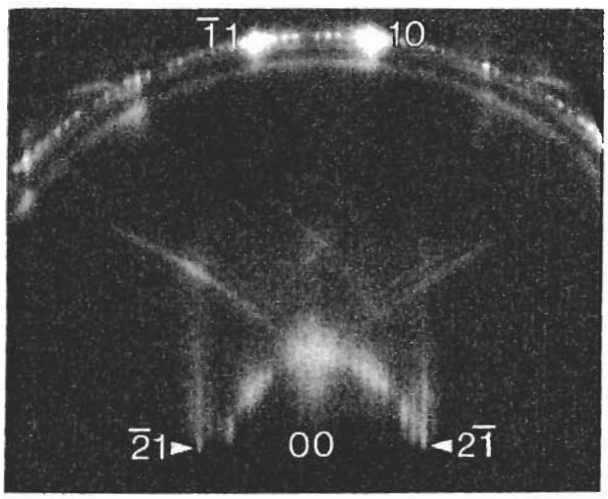

Fig.4 RHEED pattern of Mo(110) surface deposited with Nd of 1.5ML at room temperature and annealed at 1000℃. The incident electron beam is parallel to the [$\bar{1}$10]Mo orientation. The 1/11 order reflections appear between 00 and 2$\bar{1}$ Mo main reflections.

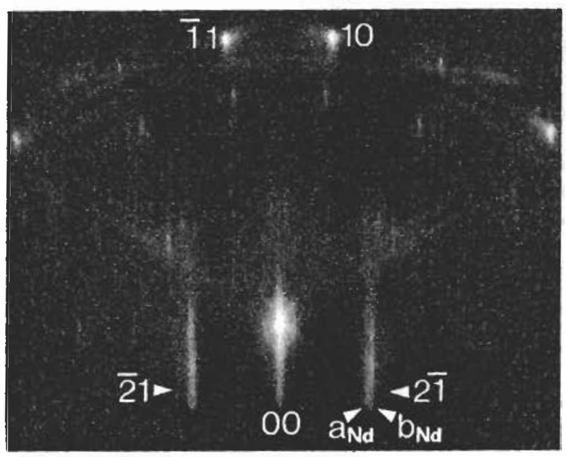

Fig.6 RHEED pattern of Mo(110) surface deposited with Nd of 2.5 ML at room temperature and annealed at 500℃. The incident electron beam is parallel to the [$\bar{1}$10]Mo orientation. Notations a_{Nd} and b_{Nd} correspond to the c(5×3) structure and (0001)Nd layer, respectively.

500℃, whose electron incidence is the [1$\bar{1}$0] orientation. The streak marked by a_{Nd} in Fig.6 appears at the same position as that marked by a_{Nd} in Fig.1, which leads to the formation of the coincident site lattice. The streak marked by b_{Nd} appears at just outside of the a_{Nd} diffraction rods, two streaks being observed as doublet.

These doublet streaks arise from diffractions of two kinds of surface structures, one is the c(5×3) structure which is just the same structure as the 1ML deposition and the other is the surface structure of bulk Nd(0001) plane. The reciprocal lattice of these structures is shown in Fig.7. The c(5×3) structure is represented by b_1* and b_2* vectors and bulk Nd(0001) structure is represented by c_1* and c_2*

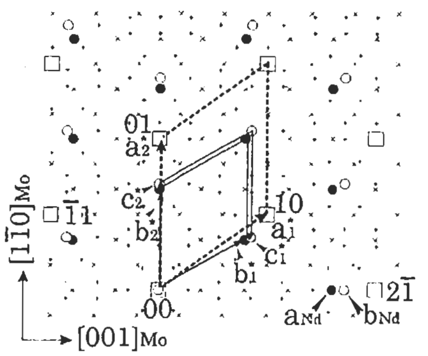

Fig.7 The reciprocal lattice obtained from the RHEED pattern shown in Fig.6. Squares indicate reciprocal rods of Mo. Filled circles and open circles indicate reciprocal rods of c(5×3) structure and (0001)Nd layer, respectively.

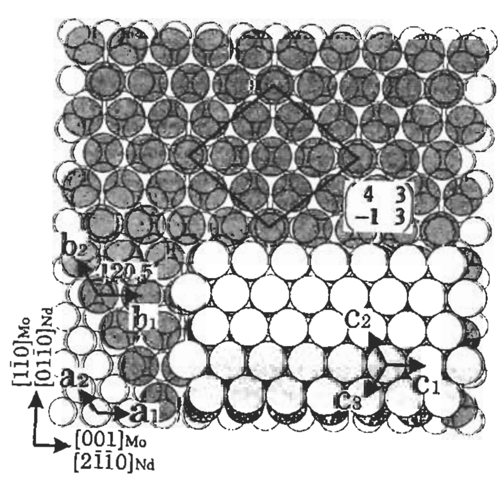

Fig.8 Real lattice model of the Nd double layer grown on Mo(110) surface. Open circles indicate substrate atoms. Filled circles and dark circles indicate the c(5×3) structure and the (0001)Nd layer, respectively.

vectors. The real lattice of these structures deduced from the reciprocal lattice are shown in fig.8. The length of the unit vectors c_1 and c_2 are 3.66 Å, which is just consistent with the atomic distance of the Nd(0001) plane. Such doublet structure appears at the deposition thickness more than 1.5ML and above 500℃. From these results it is clarified that the c(5×3) layer is formed as the first layer and the second layer having just Nd(0001) structure is formed. As the thickness increases, these reflections due to c(5×3) and Nd(0001) structure appear always together with the reflection of Mo main reflections, showing that the Nd film grows by the Stranski-Krastanov growth mode. Contrary, in room temperature condensation the Mo reflection gradually disappears with the increase of the deposition thickness, showing that the film in this case grows by the Frank-van der Merwe growth mode.

These surface structures realized in Nd/Mo(110) deposition system such as c(5×3) structure, monolayer of bulk Nd(0001) structure and (11×2) structure are the same structures as in the Ce/Mo(110) deposition system which have been investigated by Tanaka et al. Although the surface structures appearing in submonolayer of Nd are different slightly from those in Ce/Mo deposition system [8], the similarity of these experimental results would be surprising. Also, Bauer et al. have investigated the surface structures of Gd, Tb and Eu deposited on the W(110) surface and Sm on the Mo(110) surface at room temperature using LEED, and have found the same c(5×3) structure at about 1ML deposition. Considering from these facts, the cause of the appearance of the surface structures may be attributed to the atomic radius of deposits and substrates although electronic structures of rare earth metals are similar. The atomic radius of Nd of metallic state is 1.83 Å, Ce; 1.82 Å, Gd; 1.80 Å, Tb; 1.78 Å, and Sm; 1.80 Å. The atomic radius of W and Mo is 1.37 Å and 1.36 Å, respectively. In the c(5×3) structure, Nd atoms are deformed slightly from the bulk (0001) plane to coincide with Mo lattice making coherent structure, of which the interfacial energy may be predicted to be lower energy than that of Nd(0001) structure from the discussion of the surface energy calculation [9].

4. Conclusion

1. At the thickness of 1ML, the c(5×3) surface structure appears, which is close to monolayer of hexagonal Nd(0001) plane, but is slightly deformed as the atomic distance in the $[2\bar{1}\bar{1}0]$ orientation is elongated by 7.5% and in the $[01\bar{1}0]$ orientation 5.3%.. This structure has coherent structure with the Mo(110) atomic arrangement, forming coincident site lattice expressed by $\begin{pmatrix} 4 & 3 \\ -1 & 3 \end{pmatrix}$.
2. After completion of the c(5×3) structure, the layer of bulk Nd(0001) plane appears as the second layer at the deposition thickness more than 1.5ML, whose epitaxial orientation relationship is (0001)Nd//(110)Mo, $[2\bar{1}\bar{1}0]$ Nd // [001] Mo.
3. In the room temperature condensation, the Nd grows by the Frank-van der Merwe growth mode and high temperature condensation leads to the Stranski-Krastanov growth mode.
4. By high temperature annealing, several surface ordered phase of Nd on Mo surface such as the (11×2) structure and one-dimensional ordered phases appear accompanied with the reduction of Nd atoms on the surface due to evaporation.

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