Growth, thermal stability and magnetism of Ni ultrathin films on O-3 × 3/W(1 1 1) surface

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In this study, a well ordered O-3 × 3 superstructure was prepared on a W(1 1 1) surface for the investigation of the growth, thermal stability and magnetism of Ni ultrathin films on it. During the deposition and thermal annealing, Auger signal of oxygen was nearly invariant, indicating that the oxygen played a role of surfactant in this system. Due to the large lattice mismatch between the Ni films and W(1 1 1) substrate (3.95%), Ni underwent an island-growth, which was considerably affected by the growth temperature. After annealing at 500–800 K, the Auger signal ratio of Ni/W significantly decreased to approximately 1, indicating the formation of 3-dimensional islands with a wetting thickness of one pseudomorphic layer. Subsequent annealing to 800–1200 K annealing led to the more serious aggregation, i.e. de-wetting of Ni layer. The 3 and 11.5 PML Ni films revealed a stable canted magnetization, which was possibly attributed to the magneto-elastic anisotropy in the Ni films.

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1. Introduction

Because of the high melting temperature and large atomic mass which may lead to considerable spin-orbital coupling, tungsten (W) has been widely used as a substrate in the field of magnetism [1,2]. For example, W(1 0 0) single crystal is utilized in commercialized low energy electron diffraction (LEED) spin-detector [2]. An Fe/W(1 1 0) ultrathin film is also applied in a newly reported spin-detector [1]. The high thermal stability of W allows cyclic cleaning of the device substrate by high temperature flashing in an ultrahigh vacuum, which leads to the thermal desorption of the adsorbate and contamination. In contrast to the widely studied W(1 0 0) and W(1 1 0) substrates, the (1 1 1)-oriented surface is seldom used for the deposition of 3d transition metals, because it reveals a relatively rough surface for the deposit atoms [3-9]. As shown in Fig. 1(a), the body-centered-cubic W(1 1 1) surface is composed of three different atomic layers at different heights, as indicated by three different colors. The lattice constant of the hexagonal lattice is 4.47 Å, much larger than that of magnetic 3d transition metals, like Fe, Co and Ni [10-16]. In this report, we focus on the Ni films, because bulk Ni reveals larger magnetostricition effect than Co and Fe do [14,17]. Due to the considerable magnetostriction effect, when Ni films are deposited on a suitable substrate, the strain of Ni films usually leads to significant modification of the magneto-crystalline anisotropy, named magneto-elastic anisotropy. This featured magneto-elastic anisotropy usually drives the magnetization of Ni films to the surface normal direction, i.e. the perpendicular anisotropy. For example, Ni films on Cu(0 0 1) reveals the perpendicular magnetic anisotropy in the coverage range between 7 and 70 atomic monolayers [15,16]. Although the lattice mismatch between the body-centered cubic W(1 1 1) and face-centered cubic Ni(1 1 1) structure is large, when the azimuthal angle is rotated by 30°, as shown in Fig. 1(c), the lattice mismatch decreases to 3.95%. However, due to the potentially large lattice mismatch and the rough W(1 1 1) surface, the Ni atoms will be forced to corrugate with the three different atomic layers of different heights on W(1 1 1) surface. Note that in Fig. 1(c), we do not imply the information about the hard sphere model and the exact Ni bonding sites, which are beyond the scope of our experimental report and need further theoretical efforts to clarify.

Structural and magnetic properties of Ni films on Cu(1 0 0) and Cu(1 1 0) with and without O surfactant assisted growth have been studied by C. Sorg et al. [18] They found that no bulk-like NiO is formed at the surface, and O stays on top of the Ni films. The present of oxygen surfactant promotes the layer-by-layer epitaxial growth [19-22]. However, A. Picone et al. observed that oxygen efficiently floats on top of the Ni film and has an “anti-surfactant” effect on
the Ni/Fe(0 0 1) interface, promoting the formation of two-layer-high islands since the first stages of growth, whereas the Ni growth on the oxygen-free Fe(0 0 1) surface proceeds in a layer-by-layer mode [23]. Therefore, in this study, based on the well-ordered O-3 × 3/W(1 1 1) substrate, we are curious about how oxygen may possibly play the role as a surfactant and influence the growth behavior and the surface morphology of Ni films. Correspondingly, due to the large magneto-elastic anisotropy of Ni, the magnetic behavior of Ni/O-3 × 3/W(1 1 1) is also an interesting issue to probe. In this experiment, the growth mode, surfactant effect, thermal stability and magnetic properties of the Ni/O-3 × 3/W(1 1 1) ultrathin films were systematically investigated. A stable canted magnetization was observed in this system, which will be valuable in the future application of W-based magnetic devices.

2. Experiment

An adsorbate superstructure, O-3 × 3 on W(1 1 1), was used in this experiment for the deposition of Ni films and the investigation of crystalline structure, magnetism, and annealing-induced evolution of surface morphology. The sample preparation and investigation were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure better than 3 × 10^-10 Torr [24]. The crystalline structure was characterized by low energy electron diffraction (LEED). The growth behavior, surface morphology and thermal stability was monitored using Auger electron spectroscopy (AES). For the preparation of O-3 × 3/W(1 1 1), the W(1 1 1) surface was firstly cleaned by cycles of thermal annealing above 2000 K. After cyclic 1400 K annealing under 1 × 10^-6 Torr O2 followed by 1400 K annealing in UHV, a well-ordered O-3 × 3/W(1 1 1) surface was prepared. The Ni films were deposited on this O-3 × 3/W(1 1 1) surface by e-beam evaporation at either room temperature (RT: 300 K) or low temperature (LT: 250 K) with a rate of approximately 0.3 PML/min. Since bcc-W(1 1 1) exposes the top three atomic layers on the surface, 3 geometric layers of adsorbate atoms are required to fully cover the W(1 1 1) surface [10,14]. Accordingly, the unit of one physical monolayer (PML) (=3 pseudomorphic layer) is used in the rest of this paper. After capping with a protective Pd layer of 2 PML, the magnetic hysteresis loops of 2.0 and 11.5 PML Ni/O-3 × 3/W(1 1 1) were ex situ measured by magneto-optical Kerr effect (MOKE) in both in-plane and perpendicular directions at room temperature [14].

3. Experimental results and discussion

3.1. Growth

Fig. 2(a) shows the primitive 1 × 1 diffraction pattern taken from the clean W(1 1 1) surface. In our previous study, the annealing process under 1 × 10^-6 Torr O2 or in UHV can result in various surface superstructure, depending on the annealing temperature. We found 1400 K is a suitable annealing temperature to form the long range ordered O-3 × 3 superstructure on W(1 1 1). Cyclic 1400 K annealing under 1 × 10^-6 Torr O2 followed by 1400 K annealing in UHV leads to a well-ordered 3 × 3 superstructure observed on the W(1 1 1) surface, as shown in Fig. 2(b). Both steps of the annealing procedure, with and without an O2 atmosphere, are essential for the 3 × 3 superstructure, because suitable annealing process can lead to desorption of the excess oxygen and provide suitable thermal energy to organize the well-ordered surface superstructure. Fig. 2(c) shows AES spectra of the O-3 × 3/W(1 1 1) surface measured before and after 2 PML Ni deposition. Before Ni deposition, the AES spectrum of O-3 × 3/W(1 1 1) surface exhibited peaks of W at 170 eV and 363 eV. Besides, the AES peak of oxygen appears at 510 eV. The possible contamination of carbon and carbon-oxides can be excluded, because the AES peak of carbon at around 272 eV is indiscernible within the noise background. This oxygen-induced 3 × 3 superstructure can be repeatedly demonstrated by the above-mentioned processes and always exhibited an AES ratio of O_{510eV}/W_{170eV} close to the value of 1/3. The required oxygen quantity and the covering rate for this O-3 × 3 superstructure is quite stable and nearly invariant in the repeated preparations. After Ni deposition, in the AES spectrum shown in Fig. 2(c), a series of Ni peaks appeared in the range of 700–900 eV. The O_{510eV} peak intensity remained nearly invariant, indicating that oxygen was not buried at the interface of Ni/W. Instead, oxygen remained on the surface top, as a surfactant. Actually in both RT and LT-deposition, the intensity of O_{510eV} was nearly the same as the signal measured before Ni deposition. This indicates that the surfactant role played by oxygen in Ni/O-3 × 3/W(1 1 1) was not affected by the low temperature of 250 K.

Fig. 2(d) shows the AES ratio of Ni/W for RT and LT-grown Ni films, plotted as a function of the deposited Ni coverage. For RT-grown Ni films on O-3 × 3/W(1 1 1), the ratio of Ni_{878eV}/W_{170eV} increased slowly when the Ni coverage increased. Furthermore, W_{170eV} signal was always observable even though the Ni coverage was thick. This implied that Ni films on O-3 × 3/W(1 1 1) underwent a 3-dimensional (3D) growth mode at RT, i.e. the island growth. Because the morphology was composed of Ni islands, in the gap areas between Ni islands, the Ni coverage on W was quite limited. So that the AES signal of W was still observable. On the other hand, for the LT-Ni films, a larger AES Ni/W ratio was observed in LT-Ni than that observed in RT-Ni. When the substrate temperature was cooled, the low substrate temperature limited the mobility of the deposited Ni atoms and prevented the large island formation, leading to a statistically more uniform Ni coverage on W(1 1 1) and a larger Ni/W AES ratio.
In a layer-by-layer grown thin film of thickness = d, the AES signal ratio of the deposit to the substrate will follow the function shown in Eq. (1) [26].

$$\frac{\text{Deposit}}{\text{Substrate}} = \frac{A_d \cdot (1 - e^{-d/\lambda_d})}{A_s \cdot e^{-d/\lambda_s}}$$  \hspace{1cm} (1)

The numerator and denominator in Eq. (1) describe the signal contributions from the deposit and the substrate, respectively. A_d and A_s are the Auger signal sensitivity of the deposit and the substrate. \(\lambda_d\) and \(\lambda_s\) are the mean free path of the excited Auger electrons from the deposit and the substrate. Our previous study on Co(O-3 × 3/W(111)) shows a AES ratio evolution, which can be described by Eq. (1) and indicates the layer-wise growth [14]. However, in the present study of Ni/O-3 × 3/W(111), the experimental data of Ni/W ratio does not follow this behavior. Instead, the following function fits the experiment data well.

$$\frac{\text{Ni}}{\text{W}} = A \cdot (1 - e^{-d/\tau_Ni})$$  \hspace{1cm} (2)

By letting the relative Auger sensitivity A as the only free parameter, the solid lines shown in Fig. 2(d) successfully fits the experimental data using Eq. (2). Since the mean free path of 100–1000 eV electron in general metallic materials is approximately 10 Å, \(\lambda_d\) and \(\lambda_s\) are set to be 3 PML in the fitting [26]. The dashed lines in Fig. 2(d), exhibiting the function of Eq. (1), significantly deviate from the experimental data. This indicates that the layer-by-layer growth is not the case of Ni films on O-3 × 3/W(111). Since the numerator and denominator in Eq. (1) describe the signal contributions from the deposit and the substrate respectively, the successful fitting by Eq. (2) implies that the AES signal from the substrate did not change considerably with the deposited Ni coverage, i.e. the exposed surface area of W-substrate was small but nearly invariant. These fitting results also support the 3D island growth of Ni on O-3 × 3/W(111).

As it is known, three different mechanisms of film growth can be considered in terms of free energy of the film-substrate system [27]. The free energy \(\Delta \gamma\) is described by the expression \(\Delta \gamma = \gamma_s + \gamma_f - \gamma_i\), where \(\gamma_s\) is the surface energy of the substrate, and \(\gamma_i\) and \(\gamma_f\) are energy of the interface and the growing film, respectively. When the free energy \(\Delta \gamma \geq 0\), a layer-by-layer growth is implemented. In contrast to the considerable difference in RT and LT-Ni films, our previous study on Co(O-3 × 3/W(111)) exhibited no observable difference between the RT and LT-Co films. That is because, in contrast to the island growth of Ni films, Co undergoes a more uniform 2-dimensional growth, which is also supported by our previous investigation by scanning tunneling microscopy. When the free energy \(\Delta \gamma > 0\), then three-dimensional agglomerates are formed on the substrate at once (mechanism Volmer–Weber). Kolarčíkiewicz and Bauer reported on the Stranski–Krasanov growth mode in Ni/W(111), which is also consistent with our observation in Ni/O-3 × 3/W(111) [3]. In general, the real conditions are non-equilibrium, and besides of the above energies it is necessary to take into account the energy of the stresses in range of the film and its interface with the substrate, and also kinetic factors that speed up or slow down the moving to the thermodynamic equilibrium. As shown in Fig. 1, the lattice mismatch of Ni/W(111) = 3.95%, much larger than that of Co/W(111) (=2.76%) [14]. The larger lattice mismatch between Ni and W results in the large strain in the initial growth of Ni on W(111) and gradually leads to the dislocation defects, strain relaxation and the island growth mode. Because of the island growth, Ni deposition on O-3 × 3/W(111) surface gradually destroyed the 3 × 3 superstructure. When the Ni coverage is above 1 PML, there was no observable LEED spots. Accordingly, we do not have experimental evidence for the build-up of defects and strain relaxation in this system.
However some other systems of epitaxial Ni films can provide us more ideas about the possible critical strain of thickness. In Ni/Cu(100), the lattice mismatch = 2.6%; strain relaxation starts after ~3 nm [25]. In Ni/Cu/Au(100), the lattice mismatch = 6.1%, strain relaxation starts after 8 atomic monolayers (~1.4 nm) [16]. In the present system of Ni/W(111), the lattice mismatch = 3.95%. Due to the rough W(111) surface and large lattice mismatch, the island growth of Ni set up at least after ~1 PML, i.e., ~3 pseudomorphic layers, as indicated by our observation of AES ratio with variable growth temperature. The set-up of island growth may also imply the possible early strain relaxation in this system.

3.2. Thermal stability

Structural and magnetic properties of Ni films on Cu(100) and Cu(110) with and without oxygen-surfactant assisted growth have been studied by C. Sorg et al. [18] They found that no bulk-like NiO is formed at the surface, and oxygen always stays on top of the Ni films. H. L. Meyerheim et al. show an opposite view that surfactant action is ascribed to an oxygen-enriched zone extending over the two topmost layers, not only the top most layer [22]. Furthermore, A. Picone et al. observed that oxygen efficiently floats on top of the Ni film and has an “anti-surfactant” effect on the Ni/Fe(001) interface, promoting the formation of two-layer-high islands since the first stages of growth, whereas the Ni growth on the oxygen-free Fe(001) surface proceeds in a layer-by-layer mode [23]. Based on these previous reports, the oxygen-surfactant effect on growth behavior significantly diverges in different systems. In the above section, we discuss about the growth mode of Ni films on O-3 × 3/W(111). Our observation is similar to the “anti-surfactant” effect on the Ni/Fe(001). No obvious evidence suggests that the oxygen-surfactant changes the Ni growth toward 2-d layer-by-layer growth. Although the oxygen remained on the surface top of Ni/W(111), playing the role as a surfactant, the Ni films still underwent the 3-d island growth. The large lattice mismatch between Ni and W might be the main reason prohibiting the layer-wise growth. Furthermore, so far there are only few results reporting about the thermal stability of Ni films with oxygen-surfactant system. In our previous study on Co/W(111), oxygen-surfactant played an important role in both growth mode and thermal stability [3,14]. Accordingly, how the oxygen-surfactant affects the thermal stability of Ni/W(111) films was investigated in this experiment.

For the RT-grown Ni films on O-3 × 3/W(111), Fig. 3 shows AES signal of Ni848 eV, W170 eV, C270 eV and O512 eV measured at RT after annealing at various temperature (Ta) for 30 s. The Ni848 eV signal decreased when the annealing temperature was increased. Meanwhile, the W170 eV signal increased when the annealing temperature was increased. Fig. 5(a) summarizes the AES ratio of Ni848 eV/W170 eV, plotted as a function of Ta for the RT-grown Ni films. The Ni848 eV/W170 eV ratio decreased to approximately 1 while the annealing temperature was around 800 K, and then dropped to nearly zero while the annealing temperature reached 1200–1400 K. The considerable decrease of Ni848 eV/W170 eV ratio indicates that after high temperature annealing, Ni atoms aggregate and form 3D islands distributed on W(111) surface. With the surface-distributed Ni 3D islands, the effective cross section of Ni was significantly reduced and more W surface was exposed to the surface, leading to the decrease of Ni signal and increase of W signal.

Fig. 4 shows AES signal of Ni848 eV, W170 eV, C270 eV and O512 eV measured at LT after annealing at various temperature (Ta) for 30 s. Interestingly, in Figs. 3 and 4, the oxygen O512 eV signal remained nearly invariant after annealing. Because there was almost no observable carbon C272 eV signal, the origin of oxygen signal from the possible contamination of carbon-oxide can be excluded. This observation of the invariant O512 eV signal indicates that oxygen still stays on top surface, no matter how the morphology of Ni films

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**Fig. 3.** AES signals of Ni848 eV, O512 eV and W170 eV plotted as functions of annealing temperature for n PML RT-grown Ni on O-3 × 3/W(111) surface.

**Fig. 4.** AES signals of Ni848 eV, O512 eV and W170 eV plotted as functions of annealing temperature for n ML LT-grown Ni on O-3 × 3/W(111) surface.
evolved with the annealing temperature. For the LT-grown Ni, as shown in Fig. 4(a), a low coverage Ni film of 1 PML showed quick drop of Ni$_{848\text{ eV}}$ signal after 500 K annealing, revealing a similar tendency to that of RT-films. However, for thicker films of 2 and 4.7 PML LT-Ni, as shown in Fig. 4(b) and (c), the Ni$_{848\text{ eV}}$ signal was nearly invariant or even slightly increased after 500 K annealing and then significantly decreased after 750 K annealing. Fig. 5(b) summarizes the AES ratio of Ni$_{848\text{ eV}}$/W$_{170\text{ eV}}$ as a function of $T_a$ for the LT-grown Ni films. The monotonic decrease of Ni/W ratio in Fig. 5 after $T_a = 600$–$700$ K clearly indicates a transition from a 2D-like metastable layer to the large 3D stable islands, with the release of energy stored in the metastable 2D-like layer. The increase in the Ni/W AES ratio at $d = 4.7$ PML and $T = 300$–$500$ K shows that the two-dimensionality of the film increased. As discussed in the previous section and Fig. 2, LT-deposited Ni films revealed a statistically more uniform film, which might strengthen the thermal stability of the Ni films around 500 K. When the annealing temperature was up to 750–800 K, similar to the behavior of RT-films, the LT-grown Ni films underwent significant aggregation, showing a small Ni/W ratio which was $\approx 1$ at 750 K and then gradually decreased to zero with increasing $T_a$.

Fig. 6 shows the MOKE hysteresis loops of 2 PML Pd covered RT-grown 3 and 11.5 PML Ni films on O-3 × 3/W(111) measured in-plane and perpendicular directions. The remaining slope after coercivity might originate from the Pd capping layer, which is paramagnetic or possibly polarized at the interface by the Ni underlayer. The co-existence of hysteresis loops in both directions indicates the magnetization of Ni is obliquely orientated. For the 3 PML Ni film, the in-plane magnetic coercivity ($H_c$) is $7 \pm 1$ Oe and the perpendicular $H_c$ is $20 \pm 4$ Oe. Due to the larger magnetic anisotropy in a thicker film, the 11.5 PML Ni film revealed larger $H_c$ in both directions; in-plane $H_c = 20 \pm 2$ Oe and perpendicular $H_c = 46 \pm 2$ Oe. In both Ni films, the perpendicular $H_c$ is approximately 2–3 times of the in-plane $H_c$. With a simplified single domain model, this implies that the easy direction is close to the surface plane rather than the surface normal direction [28]. This observed oblique magnetization of Ni/O-3 × 3/W(111) is in contrast to the stable in-plane magnetization of Co/O-3 × 3/W(111) [14]. There are two possible mechanisms driving the Ni magnetization to an oblique direction. First, the magnetic moment of Ni (approximately 0.6 $\mu_B$/atom) is much smaller than that of Co (approximately 1.8 $\mu_B$/atom) [15,16]. Because the shape magnetic anisotropy ($E_{\text{shape}}$) of a thin film is proportional to the square of magnetic moment ($M$), i.e. $E_{\text{shape}} = -2\pi M^2$, and prefers the in-plane easy direction, the small magnetic moment of Ni apparently weakens the in-plane shape magnetic anisotropy, which actually dominates the stable in-plane magnetization of Co films. Second, in contrast to Co and Fe, Ni reveals a pronounced magnetoelastic effect, as well as its inverse effect, a large magnetoelastic anisotropy [17]. The strain induced magnetoelastic anisotropy may possibly drive the Ni magnetization toward the perpendicular direction [25]. Besides, the Pd capping layer may change the band filling and accordingly the surface magnetic anisotropy [25,29,30].
4. Conclusions

In summary, the growth, thermal stability and magnetism of Ni ultrathin films on a well ordered O–3 × 3/W(1 1 1) surface were systematically investigated in this experiment. During the deposition and thermal annealing, AES signal of oxygen is always observable and nearly invariant, indicating that the oxygen plays a role of surfactant in this system. Due to the large lattice mismatch between Ni and W(1 1 1) substrate (3.95%), Ni underwent an island-growth, which was considerably affected by the growth temperature. LT-growth can lead to a statistically more uniform film than RT-growth. After annealing at 500–800 K, the AES signal ratio of Ni/W seriously decreases to approximately 1, indicating the formation of 3-dimensional islands with a wetting thickness of nearly one pseudomorphic layer. Subsequent annealing to 800–1200 K annealing led to the more serious aggregation and destroyed the wetting layer. The 3 and 11.5 PML Ni films revealed a stable canted magnetization, which is possibly attributed to the magneto-elastic anisotropy in the Ni films. These observations of perpendicularly magnetized Ni thin films combined with a tungsten substrate will be valuable for future applications in spintronics or spin-detector-related devices.

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