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Effect of Sulfur Surface Structure on Nucleation of Oxide Seed Layers on Textured Metals for Coated Conductor Applications

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ABSTRACT

We present a study of the {100}<100> biaxially textured Ni (001) surface and oxide seed layer nucleation by *in situ* reflection high-energy electron diffraction and Auger electron spectroscopy. Our observations revealed the existence of a c(2×2) superstructure on the textured Ni surface due to segregation of sulfur contained in the bulk metal. The sulfur superstructure promotes the epitaxial (002) nucleation of seed layers such as Y_2O_3-stabilized ZrO_2 (YSZ) and CeO_2 on the metal and optimizes the biaxial texture necessary for high J_c superconductors on RABiTS.

INTRODUCTION

The RABiTS technology is based on the epitaxial growth of oxide buffer layers on a textured metal. This process is intrinsically complex because of the different chemical and electronic natures of the two surfaces involved. Changes in the atomistic structure and free energy of the metal surface determined by chemisorbed species can have a dramatic influence on the seed layer nucleation and ultimately determine the film crystallographic orientation. Although several groups have conducted accurate studies of the atomistic surfaces of d-band metals like Ni since 1960, these studies were not oriented towards understanding the heteroepitaxial nucleation of different oxide buffer layers on the metal. We were motivated to investigate the influence of surface physical and chemical properties on oxide films nucleation by inconsistencies in the seed layer texture of long lengths of RABiTS. In fact, continuous processing of meter-long tapes is much more sensitive to local imperfections than short-sample fabrication processes, in which poor-quality samples can be individually discarded.

Although several different seed layer oxides have been successfully grown on textured Ni over the past few years by different techniques[1], the previous work was based on an incomplete understanding of the Ni surface properties. In particular, the seed layer was assumed to nucleate on a clean and pure Ni surface that was obtained by annealing in forming gas before deposition[1-3].

Here we present a study of seed layer growth on {100}<100> Ni conducted using a laser ablation molecular beam epitaxy (MBE) chamber equipped with a reflection high energy electron diffraction (RHEED) system, a mass spectrometer, and a pulsed KrF excimer laser (λ = 248 nm). Using *in situ* RHEED, it was possible to monitor continuously surface structural changes during Ni substrate annealing and oxide deposition. A chemical analysis of the textured Ni surface was conducted using Auger electron spectroscopy (AES) in a separate ultra high vacuum chamber. We show that the structure and chemical composition of the textured Ni surface has a profound effect on the heteroepitaxial growth of the oxide seed layer.

EXPERIMENT

After cold rolling and recrystallization annealing[4], cube textured Ni substrates have typical grain sizes and surface roughness of 50–100 μm and 5–10 nm, respectively. The degree of grain alignment is expressed by a full width half maximum (FWHM) of 6–10° for the in-plane and out-of-plane grain boundary misorientation distributions. Previous inductively coupled plasma analyses on similar samples of Ni tape indicated the presence of C and S as major impurities in the bulk, with concentrations less than 100 and 30 wt. ppm, respectively. The samples were heated to 550 °C in high vacuum ($P_b = 1\times10^{-8}$ Torr) for one hour to remove weakly bound species that had adsorbed on the surface after air exposure. This step was sufficient to remove any trace of hydrocarbons and oxygen on the sample surface, as revealed by AES.

Characteristics of the c(2×2)-S superstructure

The RHEED patterns obtained after the heat treatment are shown in Figure 1 for two different orientations: with the incident electron beam parallel to <100> (Fig. 1a) and to <110> (Fig. 1b), respectively. Although the diffraction patterns are broadened due to the orientation distribution of the grains (the electron beam samples a few hundred grains), the RHEED streaks are well defined and distinct. The pattern in Figure 1(a) shows two extra streaks (indicated by arrows) in addition to the reflections observed for a clean Ni (001) surface pattern. The extra streaks are positioned halfway between the Ni streaks and are not observed in the <110> pattern. This situation is consistent with the presence of a c(2×2) superstructure on the {100}<100> Ni surface. Such a superstructure was observed on all the samples examined and could not be removed by annealing in vacuum, or in Ar mixed to 4% H_2 up to temperatures of 850 ºC. A superstructure-free Ni RHEED pattern was obtained by depositing a Ni overlayer *in situ* by pulsed laser deposition (PLD) from a 99.99% pure Ni target.

Auger Spectroscopy was performed on several {100}<100> Ni substrates that had been produced in different batches. All the samples investigated showed a distinct sulfur peak in the

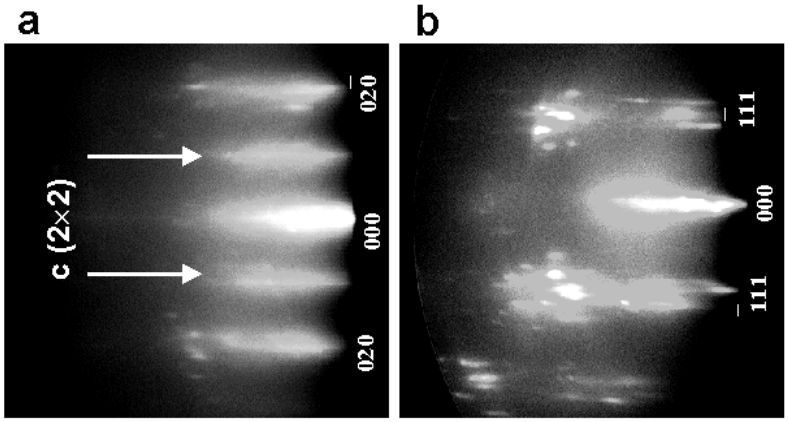

Figure 1. RHEED patterns obtained from the {100}<100> Ni surface after 1hour anneal at 500 °C with the incident electron beam along <100>, (a); and along <110>, (b). The Ni reflections are indexed and arrows indicate the superstructure streaks.

spectrum in conditions at which the superstructure was clearly visible by RHEED. The results from a typical AES experiment are shown in Figure 2. Oxygen and carbon were detected on the sample surface at room temperature but they completely desorbed after a 10-minute anneal at 550 °C. The intensity of the S signal resulted nearly constant across the sample and up to temperatures of 900 °C. The percentage of S indicated in Figure 2 was determined by the ratio between the S peak at 152 eV and the Ni peak at 61 eV corrected by the appropriate sensitivity factors. Since Auger spectroscopy is sensitive to a layer of about 5 Å, these values can differ substantially from the real atomic concentration at the surface. Subsequent studies showed that the percentage value of S measured in this temperature range corresponded approximately to a single c(2×2) layer covering the entire Ni surface[5]. A reduction in the intensity of the S peak compared to the Ni signal took place at temperature above 900°C, presumably due to S evaporation. Ion sputtering the Ni surface for 10 minutes using Ar+ ion with energy of 200 eV was sufficient to eliminate the S signal. A small carbon signal was always detected after ion bombardment, even after repeated treatments, indicating the presence of this contaminant element throughout a near-surface layer. Although the spectra acquired after ion bombardment showed traces of C, the S signal was progressively recovered after anneals in vacuum at a temperature of 430° C or higher. After a 1-h anneal at 800° C the S surface coverage returned to the previous value of ~ 0.5 ML, corresponding to one complete monolayer of c(2×2)[*]. The observation of S after annealing was associated with the decrease and ultimate disappearance of the C peak.

RESULTS

Collectively, the Auger and RHEED experiments indicate that the c(2×2) superstructure

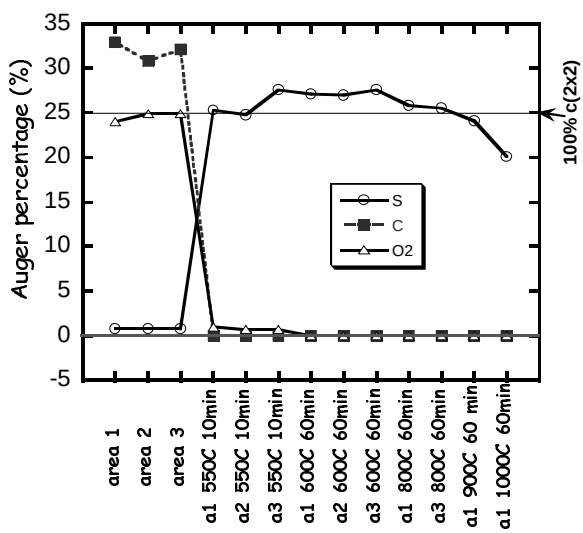

Figure 2. Percentages of the elements detected by Auger spectroscopy on {100}<100> Ni as function of annealing temperatures. The arrow on the right indicates a sulfur surface concentration of approximately 0.5 ML corresponding to complete coverage of the c(2×2).

[*] In the c(2×2) the ratio between S atoms (N_S) and Ni atoms (N_{Ni}) is 0.5. Defining 1 ML as the number of Ni atoms per unit area, a complete c(2×2) superstructure has a coverage of $\theta = N_S/N_{Ni} = 0.5$

forms after diffusion and surface segregation of sulfur atoms originating from substitutional sites in the Ni lattice. Sulfur is relatively immobile below 400° C, but can readily diffuse and segregate to the free surface during the initial Ni fabrication (e.g., during the high-temperature recrystallization anneal) [6,7]. In contrast, C atoms, which occupy Ni-lattice interstitial positions, are very mobile and desorb at lower temperatures. The surface C adatoms are displaced on formation of the S superstructure, leading to an observed depletion of surface C[6]. AES and RHEED analysis of laser deposited Ni overlayers indicated that these films did not contain any detectable amount of S superstructure. In these samples, the segregation of sulfur to the surface and the consequent formation of the c(2×2) superstructure occurred only after the sulfur atoms had diffused through the entire Ni overlayer. Formation of the sulfur superstructure on a 500 Å thick Ni film was monitored by RHEED during vacuum annealing at 750 °C and turned out to be a very slow process with a time constant of the order of 1 h or more. This justified the use of the samples with Ni overlayers as clean Ni surfaces in the seed layer deposition experiments.

Seed layer deposition

YSZ and CeO_2 seed layers were deposited by laser ablation of stoichiometric ceramic targets on the c(2 × 2)/{100}<100> Ni surface, and on the superstructure-free Ni overlayers that had been previously deposited *in situ*. The films were grown under the same conditions and with the same procedure on both surface structures, while monitoring the process with RHEED. The deposition temperature was 800° C for YSZ and 750 °C for CeO_2. In the case of YSZ, after an initial ~100-Å-thick layer was deposited in vacuum (P_{base}= 5 × 10^{-8} Torr), the O_2 partial pressure was increased to the value 1 × 10^{-5} Torr and a final 1200-Å-thick film was grown. The YSZ films grown on the c(2×2) surface showed single (002) orientation, with a (111) pole figure indicating the same degree of grain alignment as the substrate. Figure 3 shows a comparison between the RHEED pattern of an (001) YSZ single crystal with the electron beam directed along the <110>, and the RHEED pattern of a ~ 600 Å thick YSZ film on Ni with the beam along the Ni <100>. The RHEED streaks are equally spaced in the two patterns indicating that the YSZ film on Ni is (002) oriented with a 45° in-plane rotation with respect to the substrate. In contrast, the YSZ films grown on the superstructure-free Ni overlayer showed (111) orientation. The CeO_2 seed layers (~200 Å thick) were grown in a background H_2O pressure of 2.5 × 10^{-5} Torr with a ratio $P[H_2O]/P[H_2]=10^2$. Similarly to the YSZ case, the c(2 × 2) superstructure promoted (200) nucleation while deposition on the Ni surface with no superstructure resulted in (111) orientation for the CeO_2 film. The quality of the YSZ seed layers on c(2 × 2)/Ni was tested

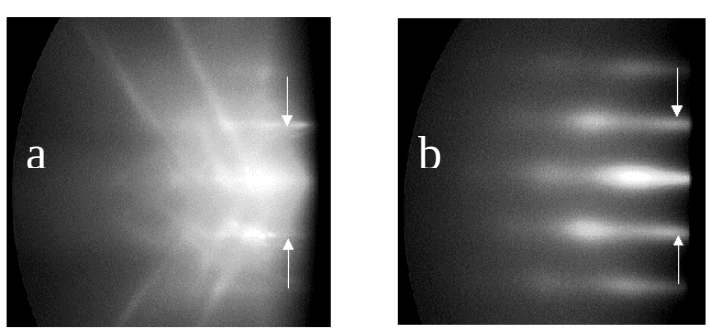

Figure 3. Comparison of RHEED patterns from a (001) YSZ crystal along <110>, (a); and an YSZ film on {100}<100> Ni along the Ni <100>, (b).

by growing a 0.3-μm-thick YBCO film by the *ex situ* BaF_2 method[8] on some of the samples. A 20-nm-thick CeO_2 cap layer enabled compatibility of the precursor layer with the YSZ. The resulting YBCO critical current density was 1.15 MA/cm^2 in self-field at 77 K, indicating that a 120-nm-thick YSZ film is a good Ni diffusion barrier and a good buffer layer for coated conductors

Although most of the Ni samples investigated showed levels of S on the surface very comparable to the values reported in Figure 2, in some cases the ratio between the S peak and the Ni peak gave rise to an Auger percentage considerably lower than 25%. For example, long texturing heat treatments at elevated temperatures caused partial evaporation of the surface S resulting in much weaker c(2 × 2) streaks in RHEED. Figure 4 shows a comparison between the (111) ϕ-scans of 2 CeO_2 seed layers deposited on Ni substrates cut from the same tape and annealed at 1100 °C for 2 and 15 h, respectively. Both CeO_2 films were cube textured and showed single (002) orientation. However, while the CeO_2 film grown on the sample annealed for 2 h replicated the substrate texture (FWHM = 8.2º), the film grown on the sample with weaker superstructure showed a broader grain alignment with a FWHM of 10.6°.

CONCLUSIONS

We believe that the role played by the S superstructure can be partially explained on the basis of structural and chemical considerations The structure of chemisorbed layers of O and S on (001) Ni has been largely investigated in the past few decades by many groups. S and O are known to be bound in the fourfold Ni hollow and to reside about 1 Å above the outer Ni plane[9-11]. Figure 5 shows a schematic of a c(2 × 2) surface structure on (001) Ni and a CeO_2 unit cell. The S layer behaves like a template that well matches and mimics the arrangement of the oxygen atoms in particular (001) oxygen sub-lattice planes of YSZ or CeO_2. S belongs to the VI group and is chemically very similar to oxygen, often exhibiting the same electronic valence. Therefore, it is plausible that during the seed layer deposition the cations easily bond to the S atoms already present on the substrate surface. We propose that during deposition, the unoccupied Ni hollows of the c(2 × 2)-S structure are filled with O, and the nucleation of CeO_2 (or YSZ) takes place starting from the S+O overlayer and continues in the sequence Ce-plane (Y+Zr-plane), O-plane, and so on, giving rise to the (001) epitaxial growth of the film, which otherwise would not take place.

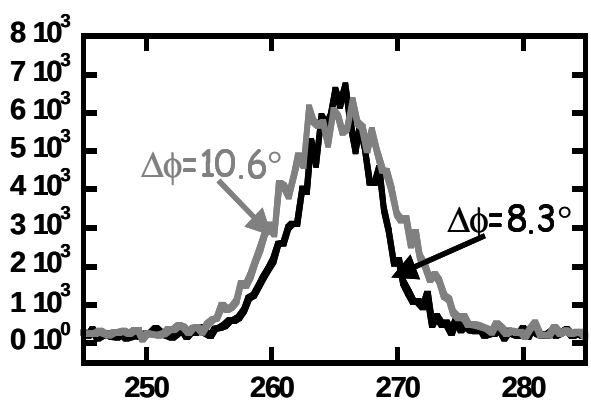

Figure 4. ϕ scans of the (111) reflection of a CeO_2 seed layer grown on a Ni substrate annealed for 2 h (black line), and on a Ni substrate annealed for 15 h (gray line).

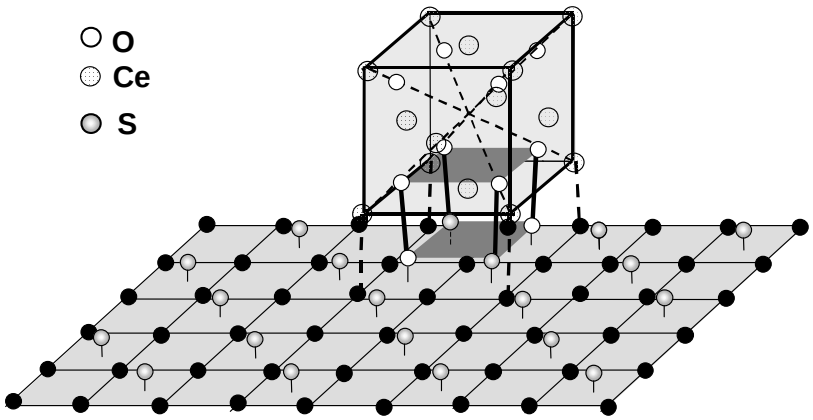

Figure 5. Proposed c(2×2) mediated epitaxial growth of CeO_2 on (001) Ni surface. The superstructure adatoms become constituents of the basal oxygen sublattice of CeO_2

textured Ni involve nucleation on a surfaces characterized by a stable c(2 × 2) sulfur superstructure. Remaining important issues for coated conductor development include the reproducibility and control of the superstructure on {100}<100> Ni and its generality with respect to other deposition methods (including solution-based approaches). Another important aspect involves the study of chemisorption-induced surface reconstruction of other metals or alloys that are potentially advantageous and more suitable for a coated conductor technology. Research to address these issues is ongoing.

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