

Controllable sealing of leaky alumina films on NiAl(100) surface by catalytic oxidation

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We show the oxide films grown by saturated dosing of oxygen on NiAl(100) is leaky, i.e., it has no apparent effect blocking deposited Co from diffusion into the bulk. We then show the easy paths for diffusion (presumably the boundaries between the oxide stripes) can be sealed by an oxidation process catalyzed by Co nanoparticles. Once sealed, the temperature range in which Co nanoparticles persist on the surface is extended by 400 K (up to 1100 K). Such "leak tight" oxide films could serve as better corrosion barrier and insulting layers. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4863406]

I. INTRODUCTION

As reported recently,^{1–6} saturated dosing of oxygen on NiAl(100) surface at 1000-1100 K can create densely packed straight stripes of ordered Al₂O₃ with very long length $(\sim 200 \text{ nm})$ and width of about 4 nm. Several different metals are found to nucleate along the boundaries between these densely packed stripes and form linear chains of monodispersed nanoparticles with size of several nanometers. The electronic and magnetic properties of these nanoparticle arrays have been extensively studied and their potential utilities as highly dispersed metal catalysts on oxides⁷⁻¹¹ are being actively explored. One interesting issue about nanoparticles is their persistence at high temperature. Sintering is one common problem that tends to increase the size and reduce the total surface area of the particles. There are cases in which sintering can be hindered.^{12,13} Another problem is diffusion of these metal nanoparticles into the substrate,^{6,7,14,15} which is particularly common when the nanoparticles consist of materials that can form bulk alloy with the substrate. This can cause total disappearance of the metal nano-particles from the surface. Our own Auger study of Co nanoparticles grown on $Al_2O_3/NiAl(100)$ is consistent with the above picture. In addition, compared with clean NiAl, we find the introduction of the striped oxide has little if any influence on the temperature dependence of the diffusion of Co into the substrate. That is, contrary to our expectation that the striped oxide could have significant effect blocking the diffusion of Co into the substrate, the oxide is actually very "leaky," presumably due to abundance of easy paths at boundaries between the oxide stripes.

In a recent scanning tunneling microscopy (STM) study of Co grown on Al₂O₃/NiAl(100), it was reported that a large fraction of Co nanoparticles can survive long time annealing at 1090 K.³ Persistence of Co nanoparticles at such high temperature is certainly very desirable as it increases the temperature limit of stable operation. However, other studies of similar systems^{6,7,14} and, in particular, our own Auger study of the same system all indicated that metal nanoparticles grown on a thin layer of oxide will sinter slightly and then completely diffuse into the NiAl substrate below 1000 K. Thus, for reasons unknown, the oxide films in Ref. 3 have become effective diffusion barriers.

For creating an anti-corrosion barrier for bulk NiAl, or an insulating layer separating nanostructures grown on top of the oxide from the substrate metal, it would be very interesting if there are ways to prepare non-"leaking" oxide films. In this work, we find the hidden mechanism that can cause sealing off of the easy path of diffusion and thus greatly enhance the thermostability of Co nano-particles. Utilizing that mechanism, we can prepare almost fully sealed oxide films that can keep their integrity even after high temperature thermal desorption of all those Co nano-particles.

II. EXPERIMENTAL METHODS

A. Apparatus and techniques

The main experiment is performed in a ultra-high vacuum (UHV) chamber¹⁶ (base pressure 1×10^{-10} Torr) that is equipped to perform temperature programmed Auger spectroscopy (TPA), thermal desorption spectroscopy (TPD), and also low energy electron diffraction (LEED) studies. TPA allows us to monitor the change of the surface compositions in real-time while the sample temperature is program- controlled. Thus, the complete temperature dependent behavior of a given sample can be recorded during any annealing process. Compared to repetitive annealing processes to higher and higher temperature and measurement after each process, TPA is not only efficient but also crucial in keeping potential residual gas contamination to a minimum.

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B. Samples preparation

Sample cleaning is by sputtering with 1.5 keV Ar⁺ ion beam and subsequent flashing to 1580 K with heating rate 5 K/s. The "striped oxide" is prepared by dosing $\sim 1000 \text{ L}$ O₂ onto a NiAl(100) held at 1000 K and then annealed at the same temperature for 3 min. Samples thus prepared have the same characteristic LEED patterns as those shown in Ref. 1. As further dosing of oxygen can hardly increase the thickness of the "striped oxide," we obtain the "thickened oxide" by first obtaining the "striped oxide" and then carry out the thickening process twice. In each thickening process, 2 nm of Al is deposited with sample at 120 K, then dose 1000 L of oxygen with sample at 300 K and finally annealing at 1000 K for 3 min. Like the "striped oxide," the "thickened oxide" also has a LEED pattern with square grid like structure, but broadened.

At the presence of Co, another way to enhance oxidation is by catalytic oxidation, in which oxygen adsorbed on Co undergoes redox reaction with substrate Al^{17-20} to form oxide. For the "catalytically grown oxide," we always start with a clean sample, form the striped oxide first, deposit Co, and then do the catalytic oxidation. Both "two-step" catalytic oxidation (dosing oxygen with sample at 300 K and then anneal to 650 K to induce redox reaction) and "one step" catalytic oxidation (dosing oxygen with sample at 650 K) have been tested, and the "one-step" process is found to be more efficient. 650 K is chosen as the diffusion of Co into the substrate is small (cf. Fig. 1(a)) while the redox reaction will proceed with a significant rate (cf. Fig. 1(b)) at this temperature.

III. RESULTS AND DISCUSSIONS

A. TPA and TPD

Figs. 1(a) and 1(b) show the Auger signal of Co (at 656 eV) as functions of sample temperature when being heated at a rate of 2 K/s (unless noted otherwise). TPA results for Co films of different initial thickness deposited on either clean NiAl(100) or NiAl(100) covered with "striped oxide" are shown in Fig. 1(a). In all these cases, Auger signals of Co have decreased close to zero when heated to 1000 K. For Co on either clean or "striped oxide" covered NiAl(100), desorption of Co has never been detected in our thermal desorption experiments even if the sample is heated up to 1600 K. For other cases in which Co do remain on the surface, as desorption of Co can be detected only above 1100 K (cf. Fig. 2), one thus deduce desorption is negligible below 1100 K. Thus, the observed drop of Co Auger signals below 1000 K can only be due to either agglomeration of Co and/or diffusion of Co into the bulk. Also, as desorption of Co is never detected for Co deposited on clean or stripe oxide covered NiAl(100), Co must have all diffused into the bulk before the temperature is raised high enough (1100 K) to induce desorption. As Co readily forms binary and ternary bulk alloys with Ni and Al,²¹ we postulate that for Co on clean NiAl(100), diffusion into the bulk occurred below 1000 K and caused the observed major drop of Co Auger signal. As it has been reported¹⁴ that Co nanoparticles grown on oxidized Ni₃Al(100) surface diffused into the bulk completely before 1000 K, we propose that in case of Co grown



FIG. 1. (a) and (b) Both show TPA curves of Co (656 eV) as functions of sample temperature. Heating rate is 2 K/s unless noted otherwise. (a) Is for Co of various thicknesses on either the clean or the "striped oxide" covered NiAl(100). (b) Shows the TPA curves for 5.8ML of Co deposited on either the "striped oxide" (green solid circle) or the "thickened oxide" (brown dotted curve). Also shown is Co on the "catalytically grown oxide" (red solid curve) and simulated Co Auger based on STM images of Fig. 3 of Ref. 3. For easy comparison, all data in (b) are normalized to their respective low temperature values. (c) Shows Auger spectra of oxygen at different stages of processing for a catalytically grown oxide. Oxygen adsorbed on Co is characterized by a very large 6 eV shift. The amount of oxygen adsorbed on Co can be reflected in the difference of Auger signals at 506 and 512 eV. For the same "catalytically oxidized sample" of Fig. 1(b), such difference (measured during the same annealing process) is shown in the inset. Clearly, the redox reaction is seen to occur in between 400 and 800 K.

on the "striped oxide" covered NiAl(100), the major drops of Co Auger signal as shown in Fig. 1(a) are also due to diffusion of Co into the bulk.



FIG. 2. This figure shows the thermal desorption rate of Co as functions of temperature when being heated at 5 K/s. All samples have 2ML of Co deposited on the "striped oxide." As shown, the total amount of Co that is observed to desorb from the surfaces depends strongly on the extent of catalytic oxidation the sample is later subject to. For the sample with no observable Co desorption, the Co must have diffused into the substrate. See text for details.

One amazing feature of Fig. 1(a) is the close resemblance of the TPA curves for Co of the same thickness but on quite different surfaces, i.e., clean NiAl(100) and the "striped oxide" covered NiAl(100). If we normalize all the curves to the low temperature value, then, within noise level, all the normalized curves overlap each other (not shown). How can the oxide have no apparent effect blocking the diffusion of Co? As shown in Fig. 3(b) of Ref. 1, Co nanoparticles preferentially nucleate along the domain boundaries in between the linear oxide stripes. It has been reported¹⁵ that when annealing Co particles on oxidized NiAl(110) surface, Co particles first disappear near the line defects and the surviving larger particles are mostly located in the middle of the domains, i.e., on the regular oxide surface. We thus postulate these domain boundaries form the easy paths for Co to diffuse through. As almost all Co nanoparticles grow right on top of one of the closely spaced domain boundaries and readily have access of the easy paths, the oxide may thus have little effect blocking the diffusion of Co. These domain boundaries have been shown to be metallic in a recent study.⁴ Although detailed atomic structure of the domain boundaries is not yet known, the resemblance of the TPA curves indicates that the energy barriers for diffusion along these easy paths are just the same as those encountered on the clean surface itself.²²

Fig. 1(b) shows the TPA curves for 5.8 monolayer (ML) of Co on the "striped oxide" (green solid circle), the "thickened oxide" (yellow dotted curve) and the "catalytically grown²³ oxide" (red solid curve). For easy comparison, the data in Fig. 1(b) have been normalized to their low temperature values. Compared with Co on the "striped oxide," Co can persist to higher temperatures on both "thickened oxide" and "catalytically grown oxide," but the catalytically grown oxide is by far much more effective, being able to extend the temperature range of persistence by about 400 K.

For "thickened oxide," LEED indicates persistence of the stripe structure, but with increased disorder. The limited effect in blocking diffusion of Co as shown in Fig. 1(b) may thus be rationalized by the existence of varied domain boundaries that provide paths slightly more difficult to pass.

Fig. 2 shows the rate of desorption of Co as functions of temperature when samples oxidized differently are being heated at the same rate of 5 K/s. For all samples, we start with growth of the "striped oxide" and then deposited with 2ML of Co. If the sample is subject to no further catalytic oxidation (solid circle, red on line), desorption rate of Co is zero, which is an evidence indicating all Co has diffused into the substrate before the temperature reached 1100 K. All the other samples have undergone different number of 2-step catalytic oxidation cycles, with each cycle consists of 1000 L of oxygen dosed at 300 K followed by annealing up to 650 K (at 2 K/s). As the number of 2-step catalytic oxidation cycles increases from 1 to 3, the amplitude of the Co desorption peak increases, indicating more Co can persist above 1100 K, which has to be the result of progressive sealing of the easy path of diffusion into the substrate. The sample (solid pink squares) that has been subjected to one two-step oxidation cycle plus a continuous catalytic oxidation process (1000 L of oxygen dosed at 650 K) is seen to have the largest desorption peak and hence is able to keep the largest amount of Co on the surface. From the area under each desorption curve, we estimate that the effect of the continuous process is approximately equivalent to 3 twostep cycles.

B. Catalytic oxidation

In the case of "catalytically grown oxide," there are many reports about what happens when exposing metal particles on Al₂O₃/NiAl(110) to oxygen. Metals that have been studied include vanadium,¹⁷ palladium,¹⁸ nickel,^{19,20} and cobalt.¹⁹ They all discovered direct or indirect evidences indicating initial capture of the oxygen on the metal nanoparticles and a subsequent redox reaction reducing the nanoparticles while oxidizing the NiAl substrate. The oxidation of NiAl increases the thickness of the alumina film progressively.¹⁸ Selective oxidation of Al is believed to be driven by the higher heat of formation for Al₂O₃ (-1678 KJ/mol) as compared to CoO (-239 KJ/mol) (for Co case). This study confirms the above picture. As shown in Fig. 1(c), after formation of the striped oxide, the oxygen Auger peak (light green curve) is at 508 eV. After deposition of Co and dosing of oxygen, the oxygen peak (red thick curve) shifts to 512 eV, which corresponds to cobaltic oxide.²⁴ Annealing to 1100 K caused the oxygen peak (brown, dotted-dashed curve) to shift to its final position of 506 eV, which corresponds to the oxygen of aluminum oxide. Further annealing to 1500 K removes the surface Co, fully exposes the aluminum oxide. The observed increase of Auger amplitude (blue, dotted curve) indicates an alumina film thicker than the striped oxide. Using the tool of TPA, the progress of the redox reaction can be easily monitored in real time by tracking the difference of the two Auger signals at 506 eV and 512 eV during an annealing process, as shown in the inset of Fig. 1(b). This TPA curve corresponds to the amount of oxygen in cobaltic oxide during the heating process. Clearly, the

redox reaction has a detectable rate at a temperature as low as 400 K and the conversion to aluminum oxide is almost complete when the temperature reached 800 K.

C. The mechanism leads to enhanced thermostability

Of more interest is the mechanism that leads to the much extended temperature range Co can persist on the catalytically grown oxide. Since the "thickened oxide" does not lead to such a dramatic effect, we propose that during the redox reaction, the easy paths for diffusion, being right under the Co nanoparticles, are somehow being sealed off. Once mostly sealed, diffusion of Co into the bulk no longer prevails and Co can last to higher temperature on the surface. Such persistence than makes it possible for Co desorption to be observed in the TPD experiments. We found the amount of Co desorbed can be varied by controlling the degree of catalytic oxidation, like Fig. 2 shows. Substrates with controlled leakage can thus be made.²⁵ Note that if we heat a sealed sample up to only 1360 K, at which all surface Co has desorbed but the oxide remains intact, then the resulting oxide film remains "sealed," as verified by the desorption behavior of a newly deposited Co layer. This also proves the persistence of Co is not due to some unusual oxidation state of the Co nanoparticle itself. We postulate the "sealed oxide film" prepared this way will be leak free to many other metals deposited on top of it. As metal nano-particles grown on the sealed oxide film cannot diffuse into the metallic substrate, such systems should better mimic metal catalyst particles dispersed on oxide matrices, especially at high



FIG. 3. The proposed scenario for the interaction of Co nanoparticles deposited on $Al_2O_3/NiAl(100)$ with and without O_2 and after annealing to 600 and 1100 K. Without oxygen, when annealed with heating rate of 2 K/s, Co nanoparticles would start sintering at 300 K, start diffusing into the substrate around 600 K and then disappear totally after 1000 K. If Co nanoparticles had been dosed with oxygen and then annealed, the redox reaction would cause further oxidation of the substrate and in the process seals up the easy paths of diffusion into the bulk. The states of Co-O under 300 and 600 K have been marked by vertical lines in the inset of Fig. 1(b). Desorption of Co starts at 1100 K. As a result, the temperature range in which Co persists on the surface can be enhanced by 400 K.

temperature. Fig. 3 shows a sketch that illustrates the proposed scenario that caused sealing.

Fig. 1(b) also shows the results of simulated Auger strength (empty blue squares) based on STM data as shown in Fig. 3 of Ref. 3. The normalized trend coincides rather well with the experimental data obtained with catalytically grown oxide. This suggests that the exceptional stability as shown in Fig. 3 of Ref. 3 is likely of similar origin.²⁶

Since domain boundaries are usually the preferred sites of nucleation for metal nanoparticles, one is lead to wonder about the generality of the observed phenomena. As the proposed scenario depends little on the specifics, it seems possible that many metal nanoparticles deposited on thin oxide films grown on various metallic substrates also have access of the easy diffusion paths at the grain boundaries of the oxides. If this turned out to be true, then the abundance of such easy diffusion paths may well become one of the major characteristics distinguishing these "model oxide surfaces" from the surfaces of real oxides. In such cases, catalytic oxidation may also be a generally effective mechanism to help control such diffusion channels. Obviously, what happens at these domain boundaries should be of crucial importance and a lot more is yet to be learned. The extremely high density of the domain boundaries of the striped oxide on NiAl(100) provides a unique opportunity for studying the phenomena that may occur on the grain boundaries of metal oxides.

IV. CONCLUSION

In summary, we have found that catalytic oxidation is by far the most effective way to extend the temperature range for Co to persist on oxide/NiAl(100) surface. As the striped oxide has little effect on restraining diffusion of Co into the bulk, we are lead to propose that the boundaries between oxide domains to be the easy paths of diffusion and sealing of such paths by catalytic oxidation caused the observed enhancement of the thermostability of Co. The resulting sealed oxide film would be a better model to oxide matrix. Generality of the phenomena among similar systems is to be assessed in the future.

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- ²⁶CO, one commonly observed residual gas in UHV chamber, causes no observable change of the TPA curve for Co.