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Influence of electron flux on the oxidation of Ni₃Al surfaces

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Electron beam currents of a few nanoamps, currently used in nanometer scale scanning Auger microscopy scanning electron microscopy, promote oxidation of polycrystalline Ni₃Al to a degree that depends on the size of the beam and subsequently on the electron flux φ_e . In fact, the oxidation of Ni₃Al at room temperature follows a model based on the premise that the electron beam creates additional nucleation sites around which oxide growth occurs. With increasing beam size the oxidation process becomes slower and O chemisorption plays a significant role. As a result the Ni-oxide depth decreases drastically with an increasing spot size (or equivalently decreasing electron flux). It offers an alternative way to monitor the NiO thickness in the nanometer range.

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I. INTRODUCTION

The growth of oxide layers on Ni and Ni/Al alloy surfaces has been the subject of a considerable number of investigations because of strong fundamental and technological interests in the fields of corrosion and catalysis.^{1–6} Furthermore, these studies are important for lithography techniques in microelectronic device fabrication,⁷ exchange-bias (ferromagnetic/antiferromagnetic) junctions,⁸ and aerospace technology.^{9,10} In particular, Ni₃Al alloys show excellent resistance to oxidation because an adherent surface oxide film is formed that protects the base metal from excessive attack.¹¹ Moreover, boron (B) doped polycrystalline Ni₃Al (~0.1–0.5 at. % B) alloys have been investigated as potential engineering materials because B appears to improve the ductility.¹¹

Although many oxidation studies have been performed on Ni^{1–6} as well as in comparison with electron beam (e-beam) stimulated oxidation,^{3,4} the oxidation of Ni₃Al(–B) surfaces under the influence of an e-beam still remains rather unexplored. Recently, it was shown that an electron beam strongly enhances the oxidation of polycrystalline Ni₃Al and Ni₃Al–B surfaces during Auger analysis at room temperature.¹² Upon beam exposure, fast oxide growth proceeds with a negligible O chemisorption regime. Fits of peak-to-peak O curves for Ni₃Al(–B) surfaces appear to support the model proposed by Li *et al.*⁴ which is based on the premise that the electron beam creates additional nucleation sites around which oxide growth occurs.

Aluminum did not participate directly in the oxidation process. The latter was consistent with room temperature (RT~300 K) studies which have shown that O chemisorbs at Ni sites or mixed Ni/Al sites without the formation of Al₂O₃, leading to a disordered surface.^{13,14} Moreover, RT scanning tunneling microscopy (STM) studies on Ni₃Al(111) surfaces indicated the formation of small oxidized nuclei. An oxide was formed that is governed by the mobility of O atoms rather than by a substantial transport of metal atoms.¹⁴

Previous studies did not examine the influence of e-beam

size effects and subsequently the influence of electron flux on the oxidation behavior of Ni₃Al(–B) surfaces (held at RT). This will be the topic of the present article, using various e-beam sizes ranging between 5 and 100 μm , in terms of *in situ* scanning Auger/electron microscopy under ultrahigh vacuum (UHV) conditions. It is also important to properly quantify e-beam effects in B segregation studies because it may alter the B distribution on surfaces/interfaces.¹²

II. EXPERIMENTAL PROCEDURE

The apparatus, described in detail elsewhere,¹⁵ consists of an UHV (base pressure $\sim 4 \times 10^{-8}$ Pa during Auger analysis) scanning Auger/electron microscope (field emission JEOL JAMP7800F). Moreover, under typical imaging conditions (accelerating voltage 10 keV, and electron beam current $I = 2.4$ nA which will be used for the e-beam induced oxidation if not otherwise stated) the attained minimum beam spot size is ~ 15 nm. Hypostoichiometric Ni₃Al–B (~24 at. % Al) samples were prepared by arc melting with a concentration of ~0.5 at. % B, and homogenized at 1100 °C (for 24 h) to manufacture an $L1_2$ ordered Ni₃Al.¹¹ All samples were ultrasonically cleaned prior to insertion into the vacuum system.

The Auger electron spectroscopy (AES) measurements were performed on polished sample cross sections which were cleaned by Ar-sputtering prior to e-beam exposure. Auger depth profile analysis was performed by Ar⁺ sputtering at a low rate ~ 0.15 nm/min calibrated with respect to Si oxide, and AES data were acquired with 400 ms dwell time (acquisition time/eV). The oxygen was provided by the UHV atmosphere (which typically contains H₂O and CO) to initiate chemisorption and direct oxidation under the influence of the e-beam. Note that during Auger maps of O the ratio (peak–background)/background from the direct spectrum is recorded.

III. OXIDATION ANALYSIS: DISCUSSION

The oxidation of Ni₃Al was described suitably¹² with the model of Li *et al.*⁴ This model is based on the premise that the incident electrons create additional nucleation sites

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FIG. 1. O peak-to-peak ($p-p$) vs the oxidation time. Data acquired with 400 ms dwell time (time/eV) and 40° tilted samples, and $I=2.4$ nA beam current. The solid lines are fits using Eq. (1). The fitting parameters are listed in Table I.

around which oxide islands grow. The oxide nucleation sites are likely to be some type of electron rich site similar to F -center anion vacancies created by sputtering a NiO surface. These sites have shown evidence of dissociative adsorption of molecular O_2 .⁴ In addition, electron impact can also cause dissociation of adsorbed water to form OH groups, which catalyze the oxidation on the surface.⁴ The oxide coverage is given by⁴

$$\Theta(t) = \Theta_{\text{sat}} - (\Theta_{\text{sat}} - \Theta_{\text{chem}}) \exp\{-Kt - (k/\varphi_e \sigma) \times [\exp(-\varphi_e \sigma t) - 1]\},$$

with φ_e the electron beam density flux ($\text{cm}^{-2}\text{s}^{-1}$), σ the electron cross section for the creation of oxide nucleation sites, t the oxidation time, and k an oxidation rate constant. The e-beam flux φ_e is estimated according to the formula $\varphi_e = I/\pi d^2/4$ assuming a circular beam spot size of an area $\approx \pi d^2/4$ (with d the e-beam diameter) and a fixed beam current $I=2.4$ nA ($1 \text{ A} = 6.25 \times 10^{18} e^-/\text{s}$). Finally, Θ_{chem} is the chemisorption saturation and Θ_{sat} the oxide saturation coverage. In terms of Auger intensities this model can be rewritten in the simple form^{4,6}

$$I_O(t) = A - (A - B) \exp\{-kt - (k/\varphi_e \sigma) [\exp(-\varphi_e \sigma t) - 1]\}$$

with A the saturated Auger intensity and B the intensity at chemisorption. This equation describes adequately the oxidation data for e-beam spot sizes $d < 30 \mu\text{m}$ (see Fig. 1 for $d=5$ and $10 \mu\text{m}$ and Table I) or significant beam fluxes ($\varphi_e > 10^{16} e/\text{cm}^2\text{s}$). Clearly, the oxidation kinetics surpasses the O chemisorption regime and fast oxide growth dominates the

oxidation process. Such an oxidation scenario has also been observed on other systems with a high affinity to O, e.g., Al(111)¹⁶ and Mg (0001)¹⁷ where oxide nucleation occurs long before the saturation of a chemisorbed coverage is reached. The direct formation of oxide nucleation centers on Ni_3Al , as was also indicated by STM studies at RT,¹⁴ is in agreement with our observation that any chemisorption is negligible whereas fast oxide growth takes place.

For e-beam sizes of $d \geq 30 \mu\text{m}$ or electron fluxes $\varphi_e < 10^{16} e/\text{cm}^2\text{s}$, the oxidation curve changes its shape and reveals a much slower oxidation process. The latter is also confirmed by the Auger map of O as is displayed in Fig. 2 where the spot intensity decays drastically with increasing e-beam size for $d > 30 \mu\text{m}$. In addition, a depth profile analysis (Fig. 3) showed that the corresponding oxide depth decreases with increasing e-beam size. In Fig. 4(a) the error bars are set equal to the Auger electron escape depth λ for O, $\lambda \approx 0.6 \text{ nm}$. The oxide depth decreases approximately linearly with the e-beam size (for $d > 10 \mu\text{m}$). However, a rather nonlinear dependence develops as a function of the electron beam density flux φ_e as is shown in the inset of Fig. 4(a).

The oxidation curves for beam sizes of $d \geq 50 \mu\text{m}$ (Fig. 1; $\varphi_e < 10^{16} e/\text{cm}^2\text{s}$) indicate an oxidation process which is characterized by chemisorption in the very beginning, followed by oxide growth (constant slope) and eventually saturation (see Fig. 1 for $d=50 \mu\text{m}$ and Table I). The formation by the beam of oxide nuclei is no longer sufficient to dominate the O chemisorption and therefore its contribution to the Auger intensity. By inclusion of a chemisorption term of the form $\sim \exp(-k_{\text{ch}}t)$ (Ref. 6) in Eq. (1), we obtain

$$I_O = A - (A - B) \exp\{-kt - (k/\varphi_e \sigma) [\exp(-\varphi_e \sigma t) - 1]\} - C \exp(-k_{\text{ch}}t), \quad (1)$$

with k_{ch} a chemisorption reaction constant. The corresponding fit using Eq. (1) is shown in Fig. 1 for the $d=30$ and $50 \mu\text{m}$ oxidation curves (for the $d=5$ and $10 \mu\text{m}$ oxidation curves the fit by Eq. (1) corresponds to $C=0$) for which the necessary saturation is reached within the exposure time scale to the e-beam. Saturation is necessary for the fit because it yields the parameter A . The fit for the $d=50 \mu\text{m}$ oxide spot indicates that O chemisorption occurs rather fast with a reaction constant larger than that of the e-beam induced oxidation, namely, $k_{\text{ch}} \approx 3k$. If we compare the second and third term in Eq. (1) we can estimate the time scale t_{ch} before which O chemisorption dominates the Auger signal,

TABLE I. Fit parameters for Fig. 1 [see Eq. (1)]. The Auger intensity is expressed in arbitrary units and thus the parameters A , B , and C also have arbitrary units. From the fit value of $\varphi_e \sigma$ we can compute the cross section σ since φ_e is known.

d (μm)	A	B	C	$\varphi_e \sigma$ (min^{-1})	k (min^{-1})	k_{ch} (min^{-1})
5	1400	131	0	$4.5 \times 10^{-2} \pm 5.3 \times 10^{-3}$	$3.4 \times 10^{-3} \pm 4.9 \times 10^{-5}$	0
10	1357	157	0	$4.2 \times 10^{-2} \pm 4.9 \times 10^{-3}$	$2.9 \times 10^{-3} \pm 4 \times 10^{-5}$	0
30	1294	393	272	$1.8 \times 10^{-3} \pm 4 \times 10^{-4}$	$3.1 \times 10^{-3} \pm 2.6 \times 10^{-5}$	$1.3 \times 10^{-2} \pm 2.6 \times 10^{-3}$
50	1164	442	307	$4.7 \times 10^{-4} \pm 1.4 \times 10^{-4}$	$2.2 \times 10^{-3} \pm 2.3 \times 10^{-4}$	$6.1 \times 10^{-3} \pm 8.4 \times 10^{-4}$

FIG. 2. SEM image of the oxidized spots with the corresponding Auger map of O. Data acquired with 100 ms at 40° tilted samples. The typical 15 nm beam spot size was used for SAM maps of O.

and thus the interaction with the specimen under e-beam exposure, being $t_{\text{ch}} \approx k_{\text{ch}}^{-1} \ln(C/A - B)$ because $\sigma \phi_e t_{\text{ch}} \ll 1$.

At any rate we point out the following for the fits in Fig. 1. The parameter A of each fit is comparable with the saturation value of the oxidation curves in Fig. 1 (A decreases for the curves of spot size from 10 to 50 μm since the oxidation is weaker as can also be seen by the Auger images of Fig. 2). The parameter B (for spot sizes $\leq 10 \mu\text{m}$; where effectively $C=0$) cannot be determined accurately since fast oxide growth takes place resulting in a value of B ($t=0$ min) within the noise level. For larger e-beam spot sizes of $d=30$ and $50 \mu\text{m}$ ($C>0$), where chemisorption starts to contribute, we have for $d=30 \mu\text{m}$ $(B-C)/A=0.094$ and for $d=50 \mu\text{m}$ $(B-C)/A=0.12$. These values are close if we con-

FIG. 3. Depth profile analysis with an e-beam spot size of 5 μm and 400 ms dwell time. The $d=5 \mu\text{m}$ spot was impossible to analyze with an e-beam spot size of 5 μm during Ar sputtering because of difficulty with spot alignment.

sider that for $d=30 \mu\text{m}$ the chemisorption regime is still rather weak to give a more precise ratio $(B-C)/A$.

The fitting parameters of the 5 and 10 μm curves in Table I are very similar, as are the curves themselves. Since there is a difference in electron flux from 5 to 10 μm , but not in

(a)

(b)

FIG. 4. (a) Oxide depth vs electron beam diameter. An almost linear dependence is revealed. The upper inset shows oxide depth vs electron beam flux density. (b) Cross section σ (extracted from the fits) vs beam spot size d .

Fig. 5. O peak-to-peak ($p-p$) vs the oxidation time. Same as in Fig. 1 but with $I=24$ nA beam current.

$\sigma\varphi_e$, it appears to be a difference in cross section. However, for both 5 and 10 μm the term $\sigma\varphi_e$ is significantly larger than k , meaning that Eq. (1) will be mainly governed by $\exp(-kt)$ after a small period of time, for large fluxes. Physically, this would mean that at sufficiently large electron fluxes the oxide growth rate is less dependent on the number of nucleation sites (which is large enough) and mainly on the present oxygen partial pressure, which is very small in this case. Therefore no matter how large the incident electron flux will be, the oxidation cannot proceed faster than a certain rate. For smaller fluxes, the creation of nucleation sites is the rate limiting factor and the speed of oxidation decreases with decreasing flux. This will lead to more inaccurate estimations of the cross sections at larger fluxes, as can be seen in Fig. 4(b), which shows the cross sections as a function of beam spot size.

In order to further quantify the effect of the e-beam flux $\varphi_e = I/(\pi d^2/4)$, a series of e-beam oxidation experiments was performed by increasing the e-beam current I with an order of magnitude (24 nA). Clearly for $d=30$ and 50 μm complete saturation is achieved as is seen in Fig. 5 in comparison with Fig. 1. The time necessary for saturation for 30 and 50 μm using 24 nA is the same as for 5 and 10 μm spots at 2.4 nA (not shown in Fig. 5) saturated at a similar time scale, confirms the assumption that the oxidation cannot proceed faster than a certain rate, in this case limited by the oxygen supply from the vacuum chamber. For $d=70$ and 100 μm the oxidation is weaker and chemisorption strongly contributes to the Auger intensity for O. This can also be visualized in Fig. 6 showing scanning electron microscopy/scanning Auger microscopy (SEM/SAM) images for the various oxidized spots. Therefore the electron flux density φ_e plays a major role in room temperature e-beam induced oxidation versus beam spot size in such a way that beyond a particular electron flux, i.e., $\varphi_e \geq 10^{16} \text{e}/\text{cm}^2 \text{s}$ for $I = 2.4\text{--}24$ nA, oxide formation is the dominant factor over O chemisorption.

Clearly in order to minimize e-beam induced oxidation, and thus to probe B segregation towards the Ni_3Al surface, the use of large beam spot sizes or effectively lower electron

Fig. 6. SEM image of the oxidized spots with e-beam current $I=24$ nA and the corresponding Auger map of O. Data acquired with 100 ms at 40° tilted samples. The typical 15 nm beam spot size was used for SAM maps of O.

fluxes ($\varphi_e < 10^{15} \text{e}/\text{cm}^2 \text{s}$) is required. This is further exemplified in Fig. 7 where a beam spot size of 100 μm has been used with O reaching saturation, as well as B displaying a significant development.

IV. CONCLUSIONS

Electron beam currents of a few nanoamps, currently used in nanometer scale scanning Auger/electron microscopy, promote oxidation of polycrystalline Ni_3Al to a degree that depends strongly on the electron flux, φ_e . In fact, room temperature oxidation of Ni_3Al follows a model based on the premise that the electron beam creates additional nucleation sites around which oxide growth occurs. However, with increasing e-beam size, d , or decreasing the electron flux, the oxidation process becomes slower with O chemisorption playing a predominant role. Since $\varphi_e \propto d^{-2}$, we can modulate

FIG. 7. B, O, Ni, and Al peak-to-peak (p - p) vs the oxidation time for an e-beam spot size $d = 100 \mu\text{m}$.

more drastically the range of electron fluxes by changing the beam size rather than the beam current I ($\varphi_e \propto I$). Because the oxide depth decreases drastically with increasing spot size, it offers an alternative way to monitor Ni-oxide thickness in a nanometer range. Such a process can be strongly relevant for the fabrication of antiferromagnetic/ferromagnetic junctions,⁸ and lithography techniques on Ni-based surfaces,⁷ as well as Ni-oxide formation for catalysis studies.¹⁻⁶ At any rate, in order to minimize e-beam induced oxidation, and thus to probe B segregation towards the Ni_3Al surface, the use of large beam spot sizes or sufficiently low electron fluxes ($\varphi_e < 10^{15} \text{e}/\text{cm}^2 \text{s}$) is required.

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