Local electron beam induced reduction and crystallization of amorphous titania films

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We report local electron beam induced reduction and crystallization of electrolytic amorphous TiO_2 films on steel at 20 keV, varying beam currents from 10 nA to 24 μA . *In situ* substrate temperature measurements and beam heating calculations demonstrate the formation of anatase (Raman) below 270 °C, clearly beneath the crystallization temperature of nonirradiated films (≈ 440 °C). The evolution of the sample current was correlated to oxide reduction via electron stimulated desorption. Atomic force microscopy revealed well defined cavities with Gaussian shape. The *e*-beam sensitivity of amorphous TiO_2 allows for patterning of macroscopic films, inducing local changes in oxidation state and phase. © 2006 American Institute of Physics. [DOI: 10.1063/1.2219398]

The unusual properties of titanium dioxide (TiO_2), such as its chemical and thermal stability, excellent optical transmittance in the visible and the near-IR range, high refractive index, high dielectric constant, *n*-type semiconducting properties, as well as its photocatalytic activity, make thin TiO_2 films attractive for wide applications.^{1–6} TiO_2 exists in the crystalline phases anatase, rutile, and brookite as well as in amorphous state (*a*- TiO_2). Oxygen loss can lead to nonstoichiometric TiO_{2-x} , $\text{Ti}_n\text{O}_{2n-1}$ magneli phases,⁷ as well as Ti_2O_3 , Ti_3O_4 , and TiO . Accordingly, the physical properties can drastically change. Changes in the oxidation state can be provoked by thermal annealing in UHV or in reductive environment, which usually creates small quantities of Ti^{3+} .^{8–10} Much larger quantities of mixed Ti oxidation states (Ti^{3+} , Ti^{2+} , Ti^+) are observed after Ar^+ bombardment.^{8,10}

Le Mercier *et al.*^{11,12} reported a drop in the electrical resistance from 10^9 to $10 \Omega \text{ cm}$ upon 335 nm laser irradiation of rutile pellets, due to the presence of Ti^{3+} and Ti^{2+} species. A significant increase of electrical conductivity was also observed after Ar, Sn, and W ion implantation into rutile.¹³ Low-density ($\mu\text{A}/\text{cm}^2$, <1 kV) electron beams¹⁰ were found to create a controlled number of Ti^{3+} defects in $\text{TiO}_2(110)$. Under transmission electron microscope (TEM) electron beam (*e*-beam) irradiation conditions, McCartney *et al.*^{14,15} observed formation of epitaxial TiO at current densities between 5 and 50 A/cm^2 and reduction beyond the monoxide after exposure of rutile single crystal samples at extremely high current densities (10^3 – $10^4 \text{ A}/\text{cm}^2$) at 100–400 kV. TiO_2 anatase powder did not show any noticeable structural or electronic changes upon TEM irradiation at 200 kV and 3 A/cm^2 .¹⁶ TEM *e*-beam heating of anodic oxides on Al, Nb, Ta, and W resulted in local crystallization of as-formed amorphous oxides, with exception of anodic TiO_2 , already crystalline after anodization.¹⁷ Recently, amorphous ZrO_2 ,¹⁸ has been *e*-beam crystallized in the TEM.

This letter reports the controlled local secondary electron microscope (SEM) *e*-beam reduction and crystallization of *a*- TiO_2 thin films deposited on macroscopic steel substrates via an electrolytic route.¹⁹ *In situ* monitored sample current and global film temperature as well as the calculated temperature rise in the *e*-beam center are correlated to reduction

and crystallization phenomena characterized *ex situ* by Raman and atomic force microscopy (AFM) measurements.

Deposition and characterization of electrolytic TiO_2 thin films on conductive substrates are described elsewhere.¹⁹ As-deposited hydrated films on mirror polished AISI 316 steel disks (ϕ of 15 mm and thickness of 1 mm) were annealed at 200 °C, well below the crystallization temperature of electrolytic TiO_2 [440 °C (Ref. 20)], to form dense *a*- TiO_2 films of ca. 100 nm thickness. TiO_2 surfaces were O_2 plasma cleaned prior to irradiation. *e*-beam irradiations were performed in a Zeiss DSM 962 SEM at 20 kV with beam currents of 24 μA , 250 nA, 30 nA, and 10 nA according to Fig. 1(a) and Table I. The samples were mounted on a heating stage (held at RT or 250 °C). A small *K*-type thermoelement was fixed in the center of the TiO_2 surface using conductive silver, and the steel substrate was fixed to the sample stage in the same way. The sample stage was electrically isolated from the SEM stage holder to allow for sample current mea-

FIG. 1. (Color online) (a) Schematic representation of irradiation conditions. The sample is mounted on the heating stage. (b) AFM images and profiles of irradiation spots: (i) 10 nA/1 s, (ii) 30 nA/3 s, (iii) 250 nA/300 s.

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TABLE I. Overview of irradiation conditions: I_p =probe current, t =irradiation time, D =probe diameter, J =current density, T_s =measured global substrate/film temperature, ΔT =additional temperature rise in probe center, and T_{tot} =total temperature in beam center.

No.	Dominating mechanism	I_p	t (s)	D (μm)	J (A cm^{-2})	T_s ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)	T_{tot} ($^{\circ}\text{C}$)	Phase
1	Reduction	4.7 μA	60/120	15	2.7	120/125	89	218/241	TiO_{2-x}
		18.6 μA		210	0.05		27		
2	Crystallization	4.7 μA	600	15	2.7	220	89	336	Anatase+ TiO_{2-x}
		18.6 μA		210	0.05		27		
3	Crystallization	4.7 μA	60	15	2.7	281	89	397	Anatase+ TiO_{2-x}
		18.6 μA		210	0.05		27		
4	Crystallization	250 nA	600	4	2	250	17	267	Anatase+ TiO_{2-x}
5	Reduction	30 nA	1–10	3	0.4	25	3	25	TiO_{2-x}
6	Reduction	10 nA	1–10	1.6	0.5	25	1	25	TiO_{2-x}

surements (Keithley 6485 picoammeter). The irradiated zones were analyzed with Raman spectroscopy in back-scattering geometry with a Renishaw Ramascope 2000 using a 633 nm HeNe laser and a spot size of 2–3 μm . AFM imaging (Topometrix Explorer) was performed in noncontact mode.

e -beam irradiation of a surface can result in radiation damage through atomic displacement, e -beam sputtering, e -beam heating, radiolysis, and electrostatic charging.²¹ Under the present conditions, radiation damage can uniquely occur from radiolysis and e -beam heating. For atomic displacement to happen, the maximum energy E_{max} transferable by an electron of mass m_e (9.1×10^{-28} g/at.) and kinetic energy E to a nucleus of mass m_a must be greater than the atomic displacement energy of the irradiated species. For nonrelativistic energies of scanning electron microscopes $E_{\text{max}} = 4E(m_e/m_a)$. With $E=20$ keV, $m_a(\text{O})=2.66 \times 10^{-23}$ g/at. and $m_a(\text{Ti})=7.95 \times 10^{-23}$ g/at., and $E_{\text{max}}=2.7$ eV (O) and 0.9 eV (Ti). The displacement energy for oxygen is much higher, 44–50 eV.²² Similarly, e -beam sputtering of surface atoms is unlikely at 20 keV.²⁹ According to Knotek and Feibelman,²³ radiolysis of transition metal oxides can occur from the incident electrons creating an inner-shell vacancy on the metal site, being followed by interatomic Auger decay from the oxygen, resulting in desorption of neutral or even positively charged oxygen ions into the vacuum.²⁴ Oxygen desorption stops as soon as the surface becomes sufficiently conductive (e.g., TiO) to stifle any further interatomic Auger decay.

The electron stimulated O desorption in α - TiO_2 is directly evidenced by the volume loss shown from AFM profiling [Fig. 1(b)]. Well defined cavities with Gaussian shape are already observed after irradiations at 10 nA/1 s, 1.6 μm in width and 17 nm in depth. Contrary to the observed pitting phenomena under TEM conditions,^{14,15} the shape of the cavities in Fig. 1(b) seems well defined, as long as no significant drift occurs during irradiation (some drift is visible after 250 nA/300 s). It is interesting to notice that the depth of 40 nm in a 100 nm thick film after 30 nA/3 s and 250 nA/300 s irradiations is almost identical. This is good evidence for the discussed reduction mechanism, which stops as soon as the reduced film becomes sufficiently conductive. A color change from yellow to dark blue was observed in all irradiation conditions, most probably due to the formation of Ti_2O_3 in the outermost oxide layer.²⁵ The full width at half maximum (FWHM) of the cavities in Fig. 1(b) were considered representative for the effective beam size at 10, 30, and 250 nA. The beam size without aperture at I_B

$=24 \mu\text{A}$ was determined using a vertical edged silicon.²⁶ The beam current distribution has a large background of almost 2 mm in diameter. It could be well represented by an overlay of two Gaussian curves, a sharp central intensity of FWHM=15.5 μm (19.7% of I_B) and a larger distribution with FWHM=209.5 μm (77.4% of I_B). Probe diameters D and the current densities J for the present conditions are given in Table I.

In Fig. 2, the absolute value of the sample current I_s upon irradiation at $I_p=30$ nA for 600 s steadily decreases from 15 to 14.7 nA. The sample current I_s is connected to the beam current I_p , the current of the backscattered electrons I_{BSE} , and the secondary electrons I_{SE} by $I_s = I_p - (I_{\text{BSE}} + I_{\text{SE}})$. Accordingly, the current decrease can be explained by an increase of I_{BSE} and/or I_{SE} . Reduction and oxygen loss will increase the average atomic mass Z in the irradiated area (Ti:47.88 and O:15.99). A maximum ΔZ of +5.3 would be expected ($\text{TiO}_2 - \text{TiO}$). Since the electron interaction volume is mostly situated in the bulk steel pellet (electron range about 1 μm at 20 keV), the backscattered electron (BSE) generation is negligibly affected by a chemical transformation in the 100 nm thin oxide film. The secondary electron (SE) yield is known to increase with increasing Z .²⁷ To exclude any change of SE and BSE yields with temperature we irradiated the pure steel pellet and found no change in sample current. Thus we can conclude that the current decrease gives direct evidence of the ongoing oxide reduction.

FIG. 2. (Color online) Evolution of global substrate/film temperature T_s (left) with and without substrate preheating under e -beam irradiation at 24 μA /600 s (TE=thermoelement). Evolution of sample current I_s (right) upon reduction during irradiation at $I_p=30$ nA. The absolute value of the negative I_s is plotted.

FIG. 3. (Color online) Laser Raman spectra of electrolytic TiO_2 films after different e -beam irradiation conditions (I_p =probe current, t =irradiation time, T_s =measured global substrate/film temperature, and T_{tot} =total temperature in beam center).

The measured global film/substrate temperature T_s upon irradiation in Fig. 2 demonstrates that the T_s without substrate preheating steadily increases from 70 to about 220 °C during irradiation at 24 $\mu\text{A}/600$ s. The initial T_s above RT is due to the slow cooling rate after an earlier irradiation at a different spot. The experiment was repeated while directly spotting on the thermoelement. With the exception of interference between beam current and thermoelement circuit, leading to an instantaneous reversible offset upon starting the irradiation, the T_s follows exactly the same behavior. It was concluded that the irradiation results in a global heating of substrate and film. The same irradiation provokes a temperature rise from 250 to 315 °C when the substrate is preheated at 250 °C [Fig. 3(b)]. For irradiations at 250 nA, only a very small T_s rise of a few degrees was observed (not shown). The additional temperature rise ΔT above bulk substrate temperature in the center of a stationary electron beam with an acceleration voltage U and a beam current I can be estimated by

$$\Delta T = \frac{3UI_p(1-\eta)}{2\pi\kappa(R_E/2 + D)}, \quad (1)$$

where η is the percentage of backscattered electrons (Fe: $\eta=0.29$), R_E is the electron range (Fe: $R_E=1.2$ μm at 20 kV), D is the probe diameter, and κ is the thermal conductivity (steel: $\kappa=22$ $\text{W m}^{-1} \text{K}^{-1}$ and TiO_2 : $\kappa=11.7$ $\text{W m}^{-1} \text{K}^{-1}$). For $D \ll R_E/2$, Eq. (1) reduces to the formula given by a derivation in Ref. 27. Since the micrometer-sized electron interaction volume is situated inside the steel pellet, the values of steel (iron) are used in Eq. (1). The calculated ΔT values and the total temperature $T_{tot}=T_s+\Delta T$ in the irradiated zones are given in Table I for all conditions. For irradiation at 24 μA , ΔT was calculated as the sum of ΔT for both Gaussian intensity distributions. Raman spectra in Fig. 3 of the irradiated spots with and without substrate preheating show the typical signature of anatase²⁸ after irradiation at 24 $\mu\text{A}/600$ s, but does not indicate crystallization after 60 and 120 s, where only an amorphous signal from TiO_{2-x} (including Ti_2O_3) and possibly remaining α - TiO_2 is measured. With sample preheating at 250 °C, a strong anatase signal is observed already after 60 s. With preheating, local crystallization can also be induced at 250 nA/600 s, which has not been ob-

served without preheating within the investigated 3000 s of irradiation. Crystallization occurs very locally, as indicated by the amorphous signal obtained ca. 8 μm away from the irradiation center. The presence of anatase in Fig. 3 is observed at T_{tot} (Table I) considerably below the crystallization temperature [440 °C (Ref. 20)] of electrolytically deposited α - TiO_2 films. In condition 4, Raman spectra showed anatase at $T_{tot}=267$ °C. A change of crystallization kinetics as a result of radiation damage under TEM conditions has been proposed by Aladjem *et al.*¹⁷ without measuring beam heating. Roddatis *et al.*¹⁸ reported the crystallization of amorphous zirconia films kept at liquid helium temperature upon intense TEM irradiation. In the present study, crystallization of electrolytic TiO_2 films on steel was possible below 270 °C. We conclude that the decrease of the crystallization temperature of more than 170 °C is a result of the intense radiation damage.

In summary, we have evidenced the possibility of controlled local reduction (thickness decrease from 100 to 60 nm) and crystallization of thin amorphous, e -beam sensitive TiO_2 films on macroscopic well conductive substrates by e -beam irradiation under SEM conditions. Using intense electron beams, these phenomena are sufficiently rapid to allow for large area high resolution patterning of amorphous valve metal oxides.

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