

Growth of amorphous Ti_2O_3 layers by laser-induced oxidation

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Amorphous Ti_2O_3 films with thicknesses $\gtrsim 10^3 \text{ \AA}$ have been obtained by cw laser irradiation of $\text{Ti}_{50}\text{Zr}_{10}\text{Be}_{40}$ exposed to low oxygen pressures. In contrast, thermal oxidation of (nonirradiated) samples reveals scales composed of crystalline oxides. Raman scattering, x-ray, and electron microscopy data on the layers are reported. It is suggested that irradiation leads to an enhanced oxidation rate preventing crystallization. Possible mechanisms of enhancement are discussed.

Amorphous oxides are commonly found in the early stages of thermal oxidation of a number of metals.¹⁻³ Because of the competing effect of crystallization, however, only very thin films (typically $\sim 5\text{--}50 \text{ \AA}$ thick) can be grown by purely thermal means.¹⁻³ Thicker layers can be obtained from other techniques, one of which is the related anodic oxidation.⁴ Oxides formed at low potentials on, e.g., Al, Ta, or Ti are found to be noncrystalline.⁵ The factors which determine the resulting amorphous or crystalline structure of a forming oxide have not been well characterized.¹⁻⁵ Nevertheless, it appears that mechanisms leading to enhanced oxidation rates (that are not accompanied by a larger increase in the rate of crystallization) should favor amorphous growth. Enhanced oxidation upon exposure to a photon flux has been recently shown for Si.^{6,7} To our knowledge, there has not been any report on the formation of amorphous oxides induced by irradiation.⁸

In our experiments, samples of the glassy-metal $\text{Ti}_{50}\text{Zr}_{10}\text{Be}_{40}$ have been exposed to oxygen pressures in the range $10^{-4}\text{--}10^{-6}$ Torr. Previously, they were etched for ~ 10 min in a solution consisting of 1 part HNO_3 and 3 parts HCl . Thermal oxidation studies involved temperatures in the $500\text{--}800\text{-K}$ range, with exposures of $5\text{--}30$ min. X-ray spectra revealed that the oxide formed consists of mostly crystalline TiO_2 , but also Ti_2O_3 and TiO . No evidence was found of the presence of Be-, Zr-, or amorphous-oxides. These results are consistent with the available data on thermal oxidation of Ti, and other Ti alloys.⁹⁻¹²

The 5309-\AA line of a cw Kr^+ laser was used to irradiate the samples. Power densities P were in the range $5\text{--}15 \text{ kW cm}^{-2}$, with the beam polarized in the plane of incidence. Lower values of P did not result in an observable oxide growth after ~ 120 min of photon exposure. The same beam served as a source to obtain Raman data from the layers. Typical results are shown in Fig. 1. Based on a comparison with a previous report on evaporated films,¹³ the broad features in the spectra are assigned to amorphous Ti_2O_3 . Electron micrographs of the samples show no inhomogeneities to the limit of resolution of the microscope ($\approx 10 \text{ \AA}$), further confirming the amorphous nature of the oxide.

The oxide signal as a function of irradiation time is shown in the inset of Fig. 1. The Raman intensity is expected to be proportional to the layer thickness (d), if $d \leq \delta$ (δ is the penetration depth of the light). Otherwise, it should not depend on d . Accordingly, the plateau that develops above $\approx 3 \times 10^3 \text{ s}$ is identified with $d \gtrsim \delta$. The optical constants of our films were not determined. However, the reflectivities

were found to be close to values reported for crystalline Ti_2O_3 ,¹⁴ i.e., $10\text{--}20\%$. This suggests that the optical properties of the amorphous and crystalline forms are likely to be similar. For the latter, $\delta \sim 10^3 \text{ \AA}$.¹⁵ This figure should be considered as a crude estimate of a lower bound for d .

The behavior of the Raman intensity before the plateau is reached shows that the oxidation rate *increases* with d .¹⁶ This is opposite to what is usually observed in pure thermal oxidation and, consequently, it implies a rate enhancement. The reflected beam intensity, also monitored during irradiation, reveals an associated increase in the power adsorbed from $\sim 45\%$ ($t = 0$) to $\sim 85\%$ in the plateau. Both effects are clearly related; the increase in the growth rate follows the rise in local temperature (T_L) due to the strong absorption of the growing oxide. We have estimated an upper limit of $T_L \sim 400 \text{ K}$ at $t = 0$, and $T_L \sim 1100 \text{ K}$ for $d \gtrsim \delta$.¹⁷ For a typical activation energy of 10^4 K , the ratio of the corresponding thermal factors is $\sim 10^7$. It is clear that such an increase in the oxidation rate will overcome any possible decrease with d associated with other mechanisms.

In the considered scheme, amorphization results from "rapid" growth at low crystallization rates. The latter condition seems to be fulfilled in our case where the estimated growth temperatures are far below the melting point of Ti oxides ($\sim 2000 \text{ K}$). The process by which an increase in d

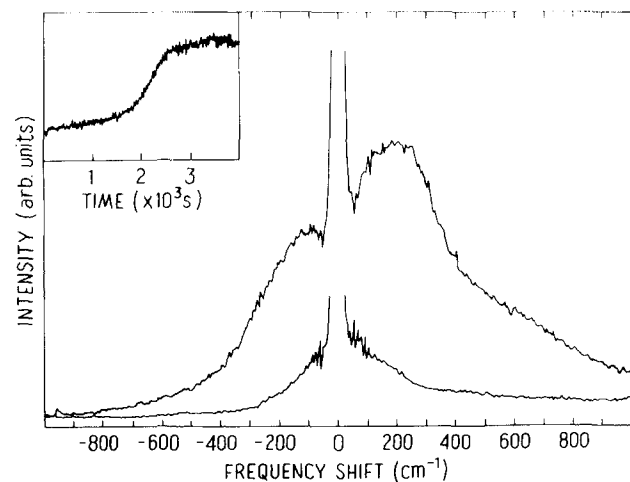


FIG. 1. Raman spectra of oxidized $\text{Ti}_{50}\text{Zr}_{10}\text{Be}_{40}$, exposed to 10^{-5} Torr, obtained before (lower trace) and after (upper trace) irradiation at $P \approx 6 \text{ kW cm}^{-2}$ (the data were taken at $P \approx 1.2 \text{ kW cm}^{-2}$). The broad band with maximum at $\sim 200 \text{ cm}^{-1}$, and the weaker feature at $\sim 620 \text{ cm}^{-1}$, are due to amorphous Ti_2O_3 . The bottom spectrum shows rotational scattering from O_2 . The oxide signal at 200 cm^{-1} vs time is indicated in the inset. The beginning of irradiation corresponds to $t = 0$.

leads to rise in T_L (which further stimulates the growth) gives oxidation rates that are "rapid" when compared to those of constant T_L oxidation. This mechanism, however, does not explain why we obtain Ti_2O_3 instead of TiO_2 , which is the dominant composition found in Ti scales.⁹⁻¹² A possibility is that the effect of irradiation on diffusion (through the generation of broken Ti-O bonds) is also important. Such an effect is not operative in TiO_2 where any absorption of 5309-Å radiation must be extrinsic.

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¹N. Cabrera and N. F. Mott, Rep. Prog. Phys. **12**, 163 (1949).

²See, e.g., A. T. Fromhold, Jr., in *Theory of Metal Oxidation*, edited by S. Amelinckx, R. Gevers, and J. Nihoul (North-Holland, Amsterdam, 1976), Vol. 1, pp. 1-9, 217-227.

³The system Al/amorphous Al_2O_3 is likely the most studied. See, e.g., K. G. Lynn, Phys. Rev. Lett. **44**, 1330 (1980); A. Bianconi, R. Z. Bachrach, S. B. M. Hagstrom, and S. A. Flodström, Phys. Rev. B **19**, 2837 (1979), and references therein.

⁴See, e.g., V. Brusica, in *Oxides and Oxide Films*, edited by J. W. Diggle (Decker, New York, 1972), Vol. 1, Chap. 1.

⁵J. Yahalom and J. Zahair, Electrochem. Acta **15**, 1429 (1970).

⁶E. M. Young, and W. A. Tiller, Appl. Phys. Lett. **42**, 63 (1983).

⁷S. A. Schafer and S. A. Lyon, J. Vac. Sci. Technol. **19**, 494 (1981).

⁸An oxide film of unusual composition was reported for Ti irradiated with 1-ms pulsed Nd laser, by A. G. Akimov, A. P. Gagarin, V. G. Dugarov, V. S. Makin, and S. D. Pudkov, Zh. Tekh. Fiz. **50**, 2461 (1980) [Sov. Phys. Tech. Phys. **25**, 1439 (1980)]. No reference to the structure of the layers was given.

⁹See, e.g., P. Kofstad, *High-Temperature Oxidation of Metals* (Wiley, New York, 1966), p. 169, and references therein.

¹⁰L. Porte, M. Demosthenous, and T. M. Duc, J. Less Common Metals **56**, 183 (1977).

¹¹T. Smith, Surf. Sci. **38**, 292 (1973).

¹²J. B. Bignolas, M. Bujor, and J. Bardolle, Surf. Sci. **108**, L453 (1981).

¹³R. J. Nemanich, C. C. Tsai, and G. A. N. Connell, Phys. Rev. Lett. **44**, 273 (1980).

¹⁴G. Lucovsky, J. W. Allen, and R. Allen, in *Physics of Semiconductors 1978*, edited by B. L. H. Wilson (the Institute of Physics, London, 1979), p. 465.

¹⁵Obtained from the data of Ref. 14.

¹⁶Data similar to ours were reported for laser-induced oxidation of Cu by M. I. Arzuov, A. I. Barchukov, F. V. Bunkin, N. A. Kirichenko, V. I. Konov, and B. S. Lu k'yanchuk, Kvantovaya Elektron **6**, 466 (1979). [Sov. J. Quantum Electron. **9**, 281 (1979)].

¹⁷The value for $d \approx \delta$ was obtained from the Raman data using Stokes-anti-Stokes ratios. The estimate at $t = 0$ was calculated from expressions given by M. Lax, J. Appl. Phys. **48**, 3919 (1977).