Optical properties of cluster-based titanium and titanium oxide films

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Abstract. The optical properties of nanostructured titanium and titanium oxide films grown on transparent substrates have been investigated. Titanium films were produced either by cluster deposition or by atom deposition, and subsequently the films were oxidised by controlled exposure to oxygen. Optical extinction spectra in the ultraviolet and visible were recorded during film growth and oxidation. Before oxidation the extinction showed the characteristics of metallic titanium, with the spectrum of the cluster-based film indicating a structure of small spherical particles. After oxidation a band gap opened up and the films became transparent in the visible, and peaks appeared in the spectrum of the sample grown by atom deposition.

1. Introduction
Traditionally properties of solid materials are controlled by the chemical composition and crystalline structure. Nanotechnology offers new possibilities to design materials properties by controlling the structure on the nanometer scale. Titanium dioxide is a material for which control of the nanostructure is important for the properties and functionality in various applications [1]. Titania has several crystalline structures of which rutile is the most stable phase for bulk and anatase is energetically favored for small particles. In applications such as photocatalysis [2] or dye-sensitized solar cells [3], the particle size is important both for stabilizing the desired crystalline form and for obtaining a porous structure with a high surface area. The bandgap of small semiconductor particles may increase due to quantum confinement, but reports regarding its presence in titania differ [4-6]. Titania particles with an appropriate size in the nm-range can be used as efficient UV-filters in sunscreens [7].

In this study we have investigated how the optical properties of thin films of titanium and titanium oxide depend on the fabrication process. Thin metallic titanium films were grown by depositing either titanium atoms or titanium clusters on a substrate. Then the films were oxidized, and the optical transmission of the films was monitored throughout the process.

2. Experimental set-up and procedures
The samples were fabricated in a flexible set-up for cluster deposition and thin-film growth [8]. For cluster deposition, a beam of clusters seeded in He gas is produced in a laser-vaporization source. The cluster beam is skimmed and passes differentially pumped chambers to reduce the pressure in the deposition chamber to $< 10^{-9}$ mbar. Just before the deposition chamber the beam passes a time-of-flight mass spectrometer. Mass spectra recorded with laser-ionization of neutral titanium clusters show that the size distribution is fairly broad, with clusters containing from tens to several hundreds of atoms, corresponding to a range of particle diameters from less than one up to a few nanometers.
Figure 1. a) Extinction spectra, optical density vs. photon energy, recorded during film growth by atom deposition and during oxidation at a substrate temperature of 625 K. The spectra recorded during and after deposition correspond to an equivalent film thickness of A: 8.5 Å and B: 17 Å. The spectra recorded during and after oxidation correspond to oxygen exposures of C: 16 L, D: 36 L, E: 3200 L, F: 1.9·10^5 L and G: 1.3·10^6 L (1 L = 1.33·10^{-6} mbar s). b) Extinction at selected photon energies in the spectra shown in a).

The deposition chamber has a resistively heated sample holder. Samples are exchanged via a load-lock system. Fused silica substrates, 10 mm in diameter and 2 mm thick, were used in this study. The sample can be rotated to face the cluster beam or a beam of atoms generated with an electron beam evaporator. The deposition rate is measured by a quartz crystal microbalance. After finishing deposition of titanium atoms or clusters, the films are oxidized by leaking O₂ into the chamber. The oxidation starts at a low pressure, in the 10^{-9} - 10^{-7} mbar range, and the pressure is increased in steps to reach high exposures after which the optical properties no longer change noticeably.

The chamber is equipped with several quartz viewports to allow for spectroscopic characterization of the samples by external sources. In this study the optical transmission was measured in the ultraviolet and visible using a fiber-optics based spectrometer. Deuterium and tungsten halogen lamps were used as light sources. The light was transmitted through an optical fiber to a mirror device focusing the beam to a 3-mm diameter spot at the center of the sample. On the other side of the chamber, a corresponding mirror device collects the transmitted light and transfers it to a spectrograph, which is a grating monochromator with a CCD detector. With the selected grating, the transmission in wavelength ranges of about 200 nm is measured consecutively.

3. Results and discussion

Optical extinction spectra of two samples grown by atom and cluster deposition, respectively, will be presented and analyzed. Figure 1a presents the optical extinction spectra in the UV for the sample grown by atom deposition. Titanium atoms were deposited onto a silica substrate at a temperature of 625 K. The deposition rate corresponded to an equivalent film thickness growth rate of 0.85 Å/minute. After 20 minutes of deposition the sample was exposed to oxygen at successively higher pressures. The optical extinction spectra are determined by comparing the transmission at the time of the measurement with the transmission of the clean substrate just before the start of deposition.

The extinction spectra recorded during the titanium film growth (spectra A and B in figure 1a) show a rather smooth extinction throughout the measured UV wavelength range. Actually, below a photon energy (E_{ph}) of 3 eV the extinction is almost constant throughout the visible range. Since the value of the optical density is practically constant in the visible in all spectra included in this study, only the UV-part of the spectra is shown here.

When the sample is exposed to oxygen (spectra C to G in figure 1a), the extinction starts to decrease in the near-UV and visible whereas it increases at the higher photon energies. The evolution
Figure 2. a) Extinction spectra, optical density vs. photon energy, recorded during film growth by cluster deposition and during oxidation at a substrate temperature of 600 K. The spectra recorded during and after deposition correspond to an equivalent film thickness of A: 2.1 Å and B: 4.3 Å. The spectra recorded during and after oxidation correspond to oxygen exposures of C: 90 L, D: 360 L, E: 2500 L and F: 6800 L. b) Extinction at selected photon energies in the spectra shown in a).

of the extinction spectra during oxidation is however not a smooth transition from the metallic film to a final oxide film, and several interesting observations can be made during the process. To facilitate the analysis of the evolution of the spectra the extinction at selected photon energies at certain times during deposition and oxidation is shown in figure 1b.

Initially (spectrum C) there is only an increase in extinction at the highest photon energies (above 5.4 eV), but as oxidation proceeds there is an increase in extinction also at lower photon energies. For example, spectrum E shows a higher extinction than B for Eph > 4.5 eV, and higher extinction than D for Eph > 4.1 eV. At the same time the decrease in extinction at the lower photon energies, appears as a uniform decrease for all photon energies below a certain value. For example, spectrum D reproduces almost exactly the shape as spectrum A below Eph = 3.6 eV (and throughout the visible range not shown here), and spectrum C has the same shape as the metallic films below Eph = 3.9 eV.

The final phase of the oxidation is, however, characterized by a significant change in the shape of the spectra. Besides the peak at about Eph = 5.8 eV, a second peak around Eph = 4.4 eV emerges and grows, and the photon energy at which the extinction start to increase shifts to lower values with a higher oxygen exposure. This evolution can easily be followed in figure 1b, where one can see that only at the highest Eph there is a constant increase in extinction, and at the lowest Eph a monotonous decrease whereas there is an initial decrease, followed by an increase for the intermediate Eph.

From these observations of the optical extinction spectra the oxidation can be described as initially proceeding as an oxidation from the surface to the core of the metallic titanium islands, since there is a significant component characteristic of metallic titanium remaining in the first two spectra (C and D). At the same time there is little structure in the part representing the oxide fraction besides an increasing extinction with a higher photon energy. During the later part of the oxidation the metallic fraction has disappeared, the threshold Eph at which there is an onset in extinction shifts to lower values and the peak at 4.4 eV grows larger. This development is consistent with the formation of an oxide close to stoichiometric TiO2 having a more ordered structure with direct interband transitions. The peak at 4.4 eV appears at a higher photon energy than the reported direct transition around 4.0 eV [5, 9], but is rather close to peaks observed for other substrate-supported thin films such as laser-deposited films [10] and nanosheets [11].

Figure 2a shows extinction spectra of the film produced by cluster deposition, at an equivalent film growth rate of 0.43 Å/minute, on a substrate at 600 K followed by oxidation, and figure 2b shows the optical density measured at selected Eph during the process.
The films of titanium clusters (spectra A and B) show an increasing extinction with increasing photon energy in the UV. This is in contrast to the film grown by atom deposition, for which an almost flat or slightly negative slope of the extinction curve was measured. The difference in the character of the spectra is likely due to different structures of the films, as indicated by comparison with calculated model spectra [8]. Small spherical titanium particles are expected to show an increasing extinction with increasing $E_{ph}$ in the UV, whereas flat particles or a continuous film would have an almost constant extinction throughout the UV. Thus, the cluster-based film likely still has a character of separate small particles, while the atom deposition is followed by diffusion leading to the formation of islands with a height smaller than their extension along the substrate [12].

When the cluster-based film is exposed to oxygen the general trends are the same as for the atom-deposition film, i.e. a decrease in the extinction for the lower $E_{ph}$ and an increase for the higher $E_{ph}$, but the evolution with time appears to be much simpler. Initially the extinction actually decreases for all $E_{ph}$, except at $E_{ph} > 5.5$ eV for which it remains constant (spectrum B to C). Then the extinction increases with an almost constant shape of the spectrum (from spectrum C to D, E and F). Below the 4 eV the extinction remains negligible in all spectra of the oxidized film, and no clear peak structure appears except for a possible maximum around 5.8 eV. The relatively simple spectra and their time evolution is probably a consequence of no well-ordered oxide with band structure being formed, i.e. there may not be a direct band gap or other strong direct transitions appearing. This would be consistent with the film maintaining a cluster character also after oxidation.

4. Conclusions
In this study it was demonstrated that the optical transmission of nanostructured titanium and titanium oxide films could be monitored in situ during film growth and oxidation. Thus, it was possible to follow the evolution of the oxide formation, and for one of the samples it could be concluded that during the oxidation there was initially a co-existence of a metallic and an oxide part, whereas a more ordered oxide formed during the later part of the oxidation.

This study also demonstrated that the optical properties of thin titanium and titanium oxide films are clearly dependent on the method by which the films were grown. The sample grown by atom deposition appeared more similar to what could be expected by thin titanium and titania films, whereas the sample grown by titanium cluster deposition maintained a character of small particles and did not show characteristics of a well-ordered oxide with band structure after oxygen exposure.

Acknowledgements
Financial support was obtained from K o A Wallenberg foundation and the Swedish Research Council.

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