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INFLUENCE OF O_2 FLOW RATE ON GROWTH RATE, COMPOSITION AND STRUCTURE OF RF-SPUTTERED TiO_X FILMS

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ABSTRACT

We have studied the influence of varying the oxygen flow rate (FO_2) on the deposition rate and composition of sub-stoichiometric titanium oxide films deposited by rf-sputtering. Rutherford backscattering is used for the composition and perfilometry for the growth rate. An abrupt reduction of the growth rate is observed for FO_2 larger than 0,050 sccm. This effect coincides with the formation of TiO_x films with x=1.78, which increases up to x=1.92 for FO_2=6 sccm. For FO_2 ~ 0.054 sccm, Ti films with about 24 at.% O content are obtained. The oxide films exhibit a mixture of the rutile and anatase TiO_2 structures (as determined by X-ray diffraction), whose relative contribution changes little with FO_2. A small but noticeable decrease of the crystallite size with increasing FO_2 can be deduced from the X-ray diffraction patterns.

1. INTRODUCTION

Nanostructured titanium dioxide is a material that finds many applications in gas sensors, photochemical solar cells and in photocatalytic water and air pollution detection and treatment. The characteristics of these devices rely on the ability of controlling the photochemistry at the oxide-fluid interface, which has been found to be quite sensitive to the specific crystalline structure[1] and composition[2] of the oxide film. One method that has been used to controllably prepare titanium oxide films with various structures and compositions is reactive sputtering deposition[3]. In this work, we have focused our attention on the influence of varying the oxygen flow rate on the composition and structure of titanium oxide films prepared by reactive rf-sputtering.

2. EXPERIMENTAL

Thin film samples were prepared by the rf-sputtering of a Ti target in Ar+O_2 atmospheres onto c-Si and glass substrates at the IFGW, UNICAMP. Thirty minutes before each deposition start, the substrates were heated to 160°C and this temperature was kept constant during the deposition runs. The varied deposition parameter was the O_2 flow rate (0.045 < FO_2 < 6.0 sccm), while the total working pressure was kept constant at 1.5×10^{-2} mbar. The target self bias was set at -1100 V. Some of the deposition runs were repeated without any intentional heating of the substrate. Under this condition, the substrates reached a steady-state temperature of ≅160°C due to plasma heating after ≈25% of the total deposition time. These samples and others deposited at different substrate temperatures are subject of a forthcoming publication.

The O/Ti mean ratio was determined by He^+ Rutherford backscattering spectrometry in normal and resonant modes of operation at the LAMFI, USP. The deposition rate was determined by perfilometry and deposition time measurements. Structural properties were determined by X-Ray diffraction.

3. RESULTS

Fig. 1 shows the deposition rate (DR) and the O/Ti ratio (x) as a function of the FO_2. It can be seen that a sharp reduction of DR occurs within a narrow FO_2 range about FO_2~0.050 sccm. This effect is accompanied by an even sharper increase in the oxygen content (x) of the films to a value of x=1.78. Interestingly, with a further two-orders of magnitude increase of FO_2, DR diminishes only slightly, with a concomitant slight linear increase of x up to a value of 1.92.

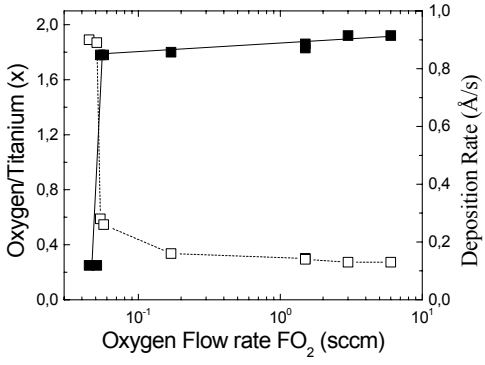

Figura 1 – Deposition rate (empty squares) and O/Ti ratio (solid squares) as a function of the oxygen flow rate.

Films deposited using FO_2 < 0.050 sccm exhibit metallic appearance but they have detectable oxygen content, as re-

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vealed by resonant elastic He^+ backscattering measurement. The corresponding spectrum for a standard sample for which a value of x=1.80 was determined from regular RBS measurement is shown together with one of the metallic samples in Fig. 2. From the ratio between the areas under the oxygen peaks observed in the spectra for the metallic film and for the standard sample, it is possible to determine an O/Ti ratio of 0.24 for the metallic sample. The larger thickness in the low x sample is responsible for the lack of the "valley" between the signals due to the Ti in the film and the Si in the substrate in this case.

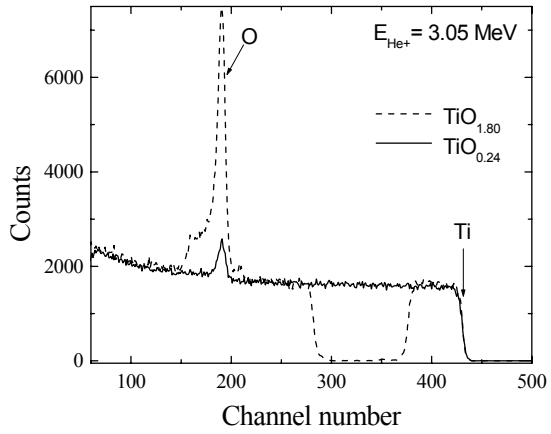

Figure 2 – Resonant elastic backscattering spectra obtained using 3.05 MeV He^+ particles incident on two different TiO_x films deposited onto Si substrates.

X-ray diffraction curves obtained from the metallic samples exhibit essentially the peaks due to polycrystalline Ti. Fig. 3 shows the X-ray diffraction curves measured for samples deposited using three different values of FO_2 > 0.050 sccm.

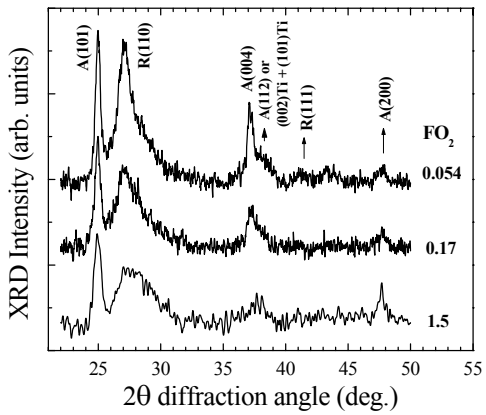

Figure 3 – X-ray diffraction patterns for three TiO_x samples deposited using three different FO_2 values. 'A' and 'R' stand for 'anatase' and ' rutile', respectively.

Diffraction peaks due to the anatase and rutile crystalline structures can be observed, which become somewhat wider as FO_2 increases. This effect is accompanied by a slight reduction of the rutile components relative to the anatase components.

Some of the depositions were repeated using exactly the same deposition conditions, except for the use of intentional heating of the substrates. The x-ray diffraction curves of these samples (not shown) have much lower contributions to the rutile component.

4. DISCUSSION

The results shown in fig. 1 can be explained by O_2 adsorption onto the sputtering target to form the TiO_2 compound, an effect that is known to drastically lower the sputtering rate from Ti targets[3]. For small FO_2 the O coverage of the Ti target is small and most of the O_2 molecules in the chamber are readily pumped away through the gettering action [4] exerted by the metallic Ti film deposited onto the chamber walls. For these flow rates, metallic Ti films with small amounts of O are obtained. As FO_2 is increased, the O coverages of both the target and the chamber walls increase. This leads to a reduction of the number of available sites for further O adsorption, and hence to a sharp reduction of the pumping action by the walls. Both effects contribute to a drastic increase of the O_2 effective partial pressure, leading to even a larger O coverage of the target, with a further reduction of the Ti sputtering rate. Hence, the Ti content in the film is rapidly reduced and approaches the stoichiometric TiO_2 composition. This behavior has been observed in other materials prepared by reactive sputtering [4].

It is interesting that the structure of the films changes little even with a large increase of FO_2 (see fig. 3). This fact is an evidence that the deposition is not kinetically limited by arrival rate of O to the substrate. This can be explained by the low Ti arrival rate at the substrate, since for such the number of O atoms needed to achieve stoichiometry is readily supplied even for very low FO_2.

The slight broadening of the diffraction peaks as observed in Fig. 3 can be interpreted as an indication for the reduction of the size of the anatase and rutile crystallites that compose the structure. A well known effect in low temperature sputtering deposition is the ion bombardment of the substrate, which significantly contributes to adatom mobility and hence to the formation of larger crystallites. We speculate that, as FO_2 increases and the lighter O atoms increasingly substitute Ar atoms in the plasma, the energy transfer per adatom due to ion bombardment decreases, leading to the formation of smaller crystallites.

5. CONCLUSIONS

The effects of varying the FO_2 in the deposition of TiO_x by reactive rf-sputtering in a O_2+Ar atmosphere on the composition, growth rate and structure of the films have been studied. A drastic reduction of the deposition rate has been observed to occur for FO_2 ~ 0.050 sccm, which coincides with a strong increase of the O content in the films, which rapidly approaches the stoichiometric TiO_2. The structure of the films for FO_2<0.054 sscm is essentially that of pure Ti, while that of the films with FO_2 exhibits a mixture of ana-

tase and rutile. The structure, growth rate and composition of the films exhibit small but noticeable changes in the $0.050<FO_2<6.0$ sccm range.

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