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Correlation between RBS, reflectometry and ellipsometry data for TiO_2 films deposited on Si

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Abstract

Using metal plasma immersion ion implantation and deposition (MePIIID) it is possible to obtain highly textured rutile layers within a wide range of stoichiometry, depending on the oxygen gas flow to titanium arc current ratio, on silicon. Even for a composition of $TiO_{1.8}$, only rutile reflections were found with X-ray diffraction. Reflectometry spectra show an internal structure of two layers with a similar density. At the same time, the layer thickness obtained from spectroscopic ellipsometry is considerable less than that from Rutherford backscattering spectroscopy (RBS), indicating that a rather abrupt transition from metallic to semiconducting is observed within the films, depending on the process conditions.

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1. Introduction

TiO_2 is a versatile and widely used material due to its outstanding optical, electrical and chemical properties [1,2]. The high temperature rutile phase is preferred for biomedical applications due to its better biocompatibility and hemocompatibility [3,4] compared to anatase polymorph. Additionally, substoichiometric variation of rutiles do exist as Magnéli phases Ti_nO_{2n-1} ($3 \leqslant n \leqslant 37$), where additional shear planes are inserted to accommodate the excess titanium [5]. Furthermore, a metallic, blueish titanium oxide phase can be obtained by ion sputtering of a rutile surface where preferential sputtering of oxygen and subsequent diffusion to the surface leads to bulk oxygen vacancies [6].

The phase formation during deposition is mainly determined by the temperature and the ion energy, yielding amorphous material at low temperature and low ion energy, e.g. evaporation techniques, while anatase is obtained in an intermediate region. Rutile can be obtained by energetic particles at room temperature ($\geqslant 10$ eV) or beyond 800 °C with thermal energies [7]. Using MePIIID, substoichiometric rutile thin films with a O/Ti-ratio between 1.5 and 1.8 were obtained [8]. In these and other investigations on TiO_2 films by MePIIID [9,10], a homogeneous film was implicitly assumed with no change of the film properties during the growth process. In this report, a detailed investigation trying to exclude or define the existence of a substructure, e.g. caused by a receding influence of the substrate or by the continuous heating of the substrate during the deposition, is presented. Beside Rutherford backscattering spectroscopy (RBS), X-ray reflectometry and spectroscopic ellipsometry (SE) were used for film characterisation.

2. Experiment

The deposition system consists of a plasma immersion ion implantation system equipped with an cathodic arc for metal ion production. A titanium cathode (purity 99.99%) was employed in the experiments with the arc

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current fixed at 100 A. A base pressure of better than 10^{-4} Pa was obtained before backfilling the chamber with oxygen at a flow of 50 sccm. The working pressure before ignition of the arc was 0.36 Pa, which decreased during the process to less than 0.1 Pa. Si(1 0 0) and Si(1 1 1) substrates were mounted at a distance of 39 cm from the cathode. The treatment time was between 120 and 300 s, with negative high voltage pulses of 30 μs length and a repetition rate of 3 kHz, i.e. a duty cycle of 9%, while the pulse voltage was varied between 0 and −10 kV. A final sample temperature between 50 and 100 °C was reached, depending on the applied voltage.

RBS measurements were performed using a 2.5 MeV He^{2+} beam at a total charge of 30 μC. The scattering angle was 170° and the surface was tilted by 40° to obtain better depth resolution. Reflectometry measurements were conducted with a high resolution diffractometer using a parallelized Cu $K_{\alpha 1}$ X-ray beam with a width of 70 μm. The resolution in Ω was 0.005°. Ex situ spectroscopic ellipsometry measurements were conducted over the spectral range from 1.5 to 5 eV using a 75 W Xe arc lamp as a light source at a fixed incident angle of 70°.

3. Results and discussion

Two different operating modes of the arc evaporator can be observed, depending on the oxygen flow rate and the arc current [8]. At high oxygen flows and low ion currents an oxygen surplus is present, leading to an oxidized cathode surface and hence a slower removal of the cathode material and less macroparticles (type 1 cathode spot, see [11]). At a higher background pressure, a saturation point is reached at an O/Ti ratio of 1.8, limiting the further uptake of oxygen from the gas. The metallic mode (type 2) was not employed in the present experiment.

Fig. 1 shows RBS spectra of films deposited simultaneously on Si(1 0 0) and Si(1 1 1) substrates at 1 kV pulse bias for 120 s. The identical spectra show the characteristic features of $TiO_{1.8}$ deposited onto Si with oxygen or carbon contamination below 1% and a sharp interface less than 50 nm. No macroparticles were found on the rather flat film [8].

The composition is $Ti_{0.36}O_{0.64}$ at a growth rate of $2–2.5 \times 10^{16}$ at./cm^{2}s, which corresponds to approximately 2 nm/s assuming the density of rutile. The titanium/oxygen ratio is constant to less than 5% deviation throughout the film with no differences observed for thicker films or films deposited at higher pulse voltages.

Reflectometry data of a different film deposited on Si(1 0 0) with the same pulse parameters but for 300 s are depicted in Fig. 2. Different models were used for simulating the data, albeit the best agreement was obtained using a four layer model TiO_x/TiO_y/TiSiO/Si. The TiSiO interface region with a thickness of 20 nm and a density of 2.8 g/cm^3 corresponds to the atomically mixed interface observed in TEM investigations [12] with a chemical mixing rather than ballistic ion mixing determining the layer thickness. The properties of the two titania sublayers were determined as a thickness of 115 and 438 nm with a density of 4.52 and 4.46 g/cm^3 for the surface and the subsurface layer, respectively.

Removal of the interface layer or assuming a continuous homogeneous titania layer led to a worsening of the fit quality as given by χ^2. Additional insertion of another layer or changing towards a gradient layer with a continuously changing density had the same effect. Allowing a variation of the roughness during the fit process leads to values between 0.3 and 1.0 nm with the highest roughness for surface layer, which are physically reasonable results.

Spectroscopic ellipsometry was employed to probe the dielectric function of films at a different wavelength region. Typical results for four samples after deposition for 300 s, at 7.5 and 10 kV pulse voltage as well as on Si(1 0 0) and Si(1 1 1) substrates are shown in Fig. 3. One immediate

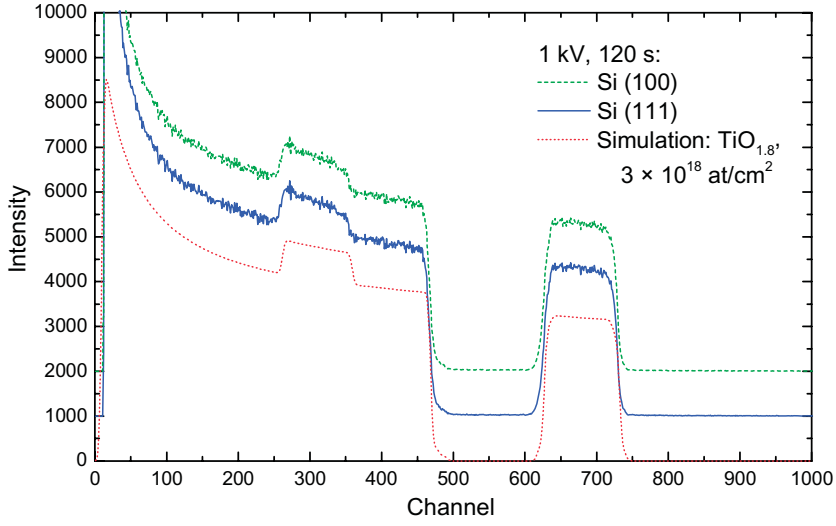

Fig. 1. RBS spectra for two samples coated simultaneously for 120 s at 1 kV pulse voltage.