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SOME PROPERTIES OF THIN FILMS OF TITANIUM MONOXIDE SYNTHESIZED BY REACTIVE EVAPORATION

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Abstract. Titanium monoxide films were deposited on silicon at temperature 300 °C by reactive evaporation. The film composition was determined by Auger electron spectroscopy (AES). X-ray diffraction (XRD) investigation of as-deposited films reveals that all films are amorphous; the resistivity of films have the relatively high value of 550 $\mu\Omega$.cm. After annealing at a temperature of 600 °C, the films were transformed into a polycrystalline *fcc* structure with a lattice parameter of 0.4166 nm. A considerable decrease of the resistivity to a value of 240 $\mu\Omega$.cm was found after the thermal treatment.

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Thin films of conductive metallic oxides are attractive candidates for low resistance contact metallization in VLSI (very large scale integrated) circuits and HTS (high temperature superconducting) devices as well as in permanent memory devices due to their high efficiency as diffusion barrier layers that prevent the deterioration of interfaces and the structure as a whole. E. g., RuO_2 exhibits low resistivity [1] together with excellent barrier properties against interdiffusion of Al and Si up to annealing temperatures of 600 °C [2, 3]. Titanium sub-oxide films are expected to have similar behaviour. It is shown that the incorporation of oxygen in titanium films slows down and even stops the extension of the $TiSi_2$ layer formed by diffusion of silicon from the wafer [4]. In these experiments, a thin layer of TiO was found at the interface between TiO_2 and $TiSi_2$.

Conductive oxide films could be of particular interest when they are associated with lead zirconate titanate (PZT) films to improve the lifetime of ferroelectric devices [5], TiO has the same cubic structure as MgO, which is a seed substrate for the epitaxy

of PZT [6]. Titanium monoxide therefore may prove to be suitable for reducing the interdiffusion and improving the nucleation of the proper phase of PZT.

It is known from the equilibrium phase diagram of the Ti/O system that there exist a number of phases (from the solid solution of oxygen in titanium up to the stoichiometric TiO_2) depending on the O-content. The titanium monoxide phase has a very narrow range of homogeneity (around 50 % O-content). The formation of thin films consisting of such an intermediate phase is a general problem in the synthesizing metal-metalloid compounds, especially when a monophase layer is required. The purpose of the study reported in this paper was the synthesis of titanium monoxide thin films by means of reactive evaporation, bearing in mind the primary importance of the structural characteristics of the film.

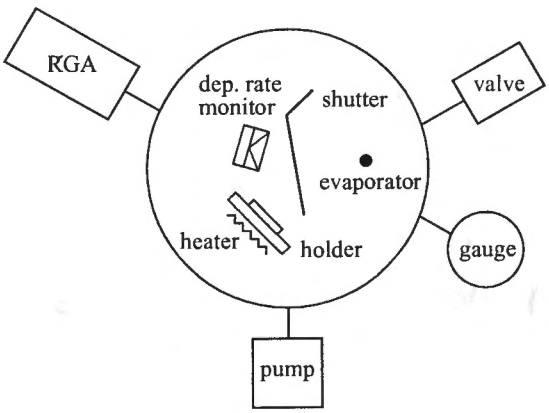

Fig. 1. Experimental setup, schematic representation

The film deposition was performed in an ultrahigh vacuum system schematically shown in Fig. 1. The titanium vapour flux to the substrate was supplied by a Ti-evaporator heated by electron bombardment. The O_2-pressure during deposition was maintained constant using an automated dosing valve. The typical deposition rate, as measured by a quartz deposition rate/thickness monitor, was 0.11 $nm.s^{-1}$. The O_2-pressure was varied in the different runs from 9×10^{-6} to 1.4×10^{-5} mbar. The O_2-pressure range was predetermined by calculations based on the available data for adsorption of oxygen on continuously deposited titanium films [7]. The base pressure prior to the deposition was about 5×10^{-6} Pa with a very low-content of light hydrocarbons in the residual gas atmosphere, registered by RGA (residual gas analyser) as an important condition for eliminating the carbon contamination of the films. Films with 340 nm thickness were deposited on *p*-type (100) oriented silicon substrates kept at a temperature of 300 °C as measured by a thermocouple. Selected films were subjected to thermal annealing at a temperature of 600 °C in an inert atmosphere.

The films composition was studied by Auger electron spectroscopy (AES). The Auger spectra were recorded in direct $E.N(E)$ mode by beam brightness modulation with a primary electron beam energy of 2 keV. Before the Auger intensities estimation,

a background subtraction was performed, the background being approximated with an analytical function of the form $A.E^m$. The Auger intensities of Ti and O were then calculated by integrating the peak areas accounting for the inelastically scattered Auger electrons using Shirley's method [8]. The phase and structure characteristics of the films were investigated by X-ray diffraction (XRD) using a θ-2θ goniometer, Co ($\lambda = 1.79021$) radiation. Resistivity measurements were carried out by the four-probe method.

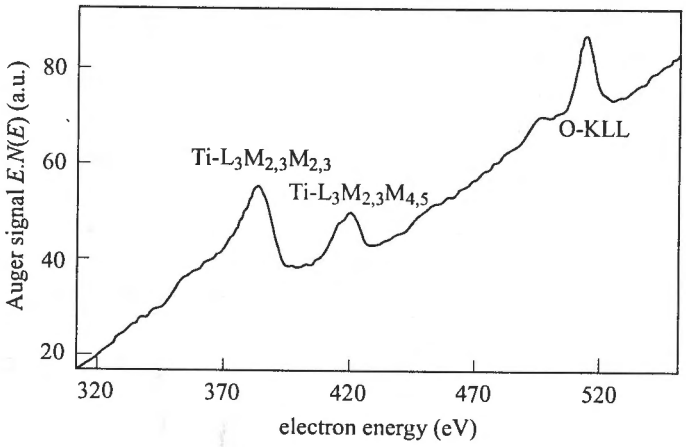

Fig. 2. Ti-LMM and O-KLL Auger peaks representative of a TiO film deposited at O_2-pressure of 1.14×10^{-5} mbar

Figure 2 shows the Auger spectrum of a film obtained at O_2 pressure of 1.14×10^{-5} mbar. The contributions to the Ti-$L_3M_{2,3}M_{4,5}$ Auger peak in the 400–430 eV energy range arise predominantly from valence band transitions, as identified by Solomon and Baun [9] in Ti, TiO and TiO_2 from a molecular orbital model [10]. The shape of the low-energy shoulder of the Ti-$L_3M_{2,3}M_{4,5}$ peak (at approximately 407 eV, Fig. 2) is distinctive of TiO [9]. The quantitative analysis of titanium and oxygen by AES is based on the integrated O and Ti peaks as representative of the titanium and oxygen by AES is based on the integrated O and Ti peaks as representative of the O/Ti concentration ratio. The O-KLL and Ti-$L_3M_{2,3}M_{4,5}$ peaks were integrated in the 470 to 529 eV and 400 to 430 eV energy ranges, respectively. The calculated value of the O-KLL/Ti-$L_3M_{2,3}M_{4,5}$ integral ratio of 1.6 identifies the film composition as corresponding to that of titanium monoxide. This was proved by a comparison of this integral ratio with reference data acquired by in *situ* Auger analysis of films deposited by ion-beam sputtering with a large range of O/Ti concentration ratio variations [11]. We observed that the deviation from the Ti-monoxide composition was quite sensitive to the O_2-pressure (actually, to the O_2-pressure/deposition rate ratio). In spite of this, we synthesized by means of reactive evaporation stable Ti-monoxide thin films whose composition remained unchanged after thermal annealing of at least 600 °C. X-ray diffraction investigation of as-deposited films reveals that at 300 °C deposition

temperature all films are amorphous. These results support an expected film growth, whereby the condensation and reaction of the species that form the compound occur with energy-deficient arriving particles, a typical condition for conventional reactive evaporation. The resistivities of the as-deposited TiO films had relatively high values, about 550 $\mu\Omega$.cm. After annealing at 600 °C the films were transformed into a polycrystalline *fcc* TiO structure with a lattice parameter of 0.4166 nm. In cubic TiO_x, the lattice parameter is expected to vary linearly with the oxygen content [12]. The value of 0.4166 nm registered in this study, when compared with the data reported in Ref. [12], is related to an oxygen content of 52 % which confirms the quantification by the AES analysis performed here. The (111) and (200) XRD-reflections were only detected in the form of very narrow peaks. As evaluated from the width of these peaks, the grain size in the film was in the range of 20 to 30 nm. After annealing, a considerable resistivity decrease to 240 $\mu\Omega$.cm was found.

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