



High k dielectrics for low temperature electronics

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Abstract

In this work the electrical and structural properties of two high k materials as hafnium oxide (HfO₂) and tantalum oxide (Ta₂O₅) produced at room temperature are exploited. Aiming low temperature processing two techniques were employed: r.f. sputtering and electron beam evaporation.

The sputtered HfO₂ films present a nanocrystalline structure when deposited at room temperature. The same does not happen for the evaporated films, which are essentially amorphous. The density and the electrical performance of both sputtered and evaporated films are improved after annealing them at 200 °C. On the other hand, the Ta₂O₅ samples deposited at room temperature are always amorphous, independently of the technique used. The density and electrical performance are not so sensitive to the annealing process. The set of data obtained show that these dielectrics processed at temperatures below 200 °C present promising properties aiming to produce devices at low temperature with improved interface properties and reduced leakage currents.

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1. Introduction

The expression transparent electronics has been associated with thin film transistors (TFT) using wide band gap oxide semiconductors as the channel layer [1–4] since they are transparent in the visible spectrum region. Materials such as zinc oxide, indium oxide or a binary or ternary mixture of them have been the most used. Most recent research has focused on improving the field-effect mobility of large gap compound semiconductors, by improving the quality of the channel materials going as far as using single crystals [5,6]. However, these approaches require high-temperature processes which are not compatible with low cost plastic-based substrates.

One of the envisaged applications of these novel TFTs is to replace hydrogenated amorphous or polycrystalline silicon TFTs that now serve as the backplane for active matrix displays whose pixels are based on liquid crystals or organic light emitting diodes. Up to now, most of these transparent TFTs have been produced using high temperature dielectrics, namely a multilayer compound

constituted aluminum oxide and titanium oxide, known as ATO, deposited by atomic layer deposition (ALD). This material was preferred due to its high resistivity ($\sim 10^{15}$) and breakdown voltage (>4 MV/cm) as well as relatively high dielectric constant (~ 16) [4]. Nevertheless, this deposition technique is not low temperature compatible. However, it seems to be imperative the use of high k materials, since by doing so thicker dielectrics can be used, without decreasing the gate capacitance, with better step coverage and a better pinhole free layer, without increasing the on voltage and reducing so the leakage currents [7], as required for high definition displays. So, the production of good high k dielectrics at low temperatures is an important step towards transparent and low cost flexible electronics.

Several materials may emerge as candidates, but they must fulfill some criteria, some of them similar to the ones required for CMOS applications. First of all, a high band gap, higher than the semiconductor is desirable, preferentially with favorable conduction band offset, to avoid high gate leakage. Also a good interface is required and since epitaxy is out of question at low processing temperatures, this can only be achieved using amorphous dielectrics. On other hand, thermal stability is not so important when thinking on low temperature processing.

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Two deposition methods that may be used to produce dielectrics films at low temperatures are sputtering and electron beam evaporation. In this work these techniques were used to produce hafnium oxide (HfO_2) and tantalum oxide (Ta_2O_5) films highlighting some advantages and disadvantages of each material.

2. Experimental details

The samples prepared by r.f. magnetron sputtering were deposited from 3 inch HfO_2 and Ta_2O_5 targets at a pressure of 2 Pa, an O_2/Ar ratio of 0.2 and a r.f. power of 150 W. The ones prepared by evaporation were deposited using oxide pellets, at an oxygen partial pressure of 5×10^{-3} Pa. Glass and crystalline $\langle 100 \rangle$ p-type silicon, that was cleaned in an HF solution and de-ionized water, were used as substrate. All samples were deposited at room temperature. The films were then annealed in an argon (Ar) atmosphere for 2 h at 200 °C. Structural analysis was done by X-ray Diffraction (XRD) using a Rigaku DMAX III-C diffractometer and by Spectroscopic Ellipsometry (SE) using a Jobin-Yvon UVISSEL ellipsometer on a spectral range between 1.5 and 5 eV and with an angle of incidence of 70 degrees. Aluminum contacts were evaporated on the back of the silicon substrates and over the deposited films (using a shadow mask) before C-V and J-V measurements. C-V measurements were accomplished at 1 MHz using $8 \times 10^{-3} \text{ cm}^2$ circular electrodes. J-V curves were plotted using a Keithley 617 programmable electrometer to evaluate the leakage current.

3. Results and discussion

3.1. HfO_2

The structure of the sputtered and evaporated HfO_2 films was investigated by XRD. The room temperature sputtered HfO_2 is nanocrystalline, as suggested by the presence of some broad diffraction peaks on the XRD patterns (Fig. 1a), with their position corresponding to the monoclinic structure, the low temperature phase of HfO_2 . After annealed for 2 h at 200 °C, the most significant modification detected on the XRD patterns is a slight shift on the peaks towards their reference position, indicating some residual stress relaxation. On other hand, the evaporated films present no peaks on the diffraction patterns meaning that they are amorphous with no changes detected by XRD after annealing (Fig. 1b).

Spectroscopic ellipsometry (SE) was also used to analyze the annealing effect on compactness and roughness of the HfO_2 films deposited over c-Si. The simulation of the experimental results was done using a 4-layer model consisting in substrate (a c-Si reference), interfacial layer (SiO_2 reference), bulk (a dispersion model to simulate the HfO_2) and surface roughness (a BEMA [8] consisting in a mixture of 50% of HfO_2 and 50% of voids). To simulate the optical behavior of nanocrystalline materials with no significant long range order, a dispersion model developed for amorphous films was used [9,10]. The best fitting results were achieved using the classical Lorentz oscillator and the goodness of the fit is obtained by mini-

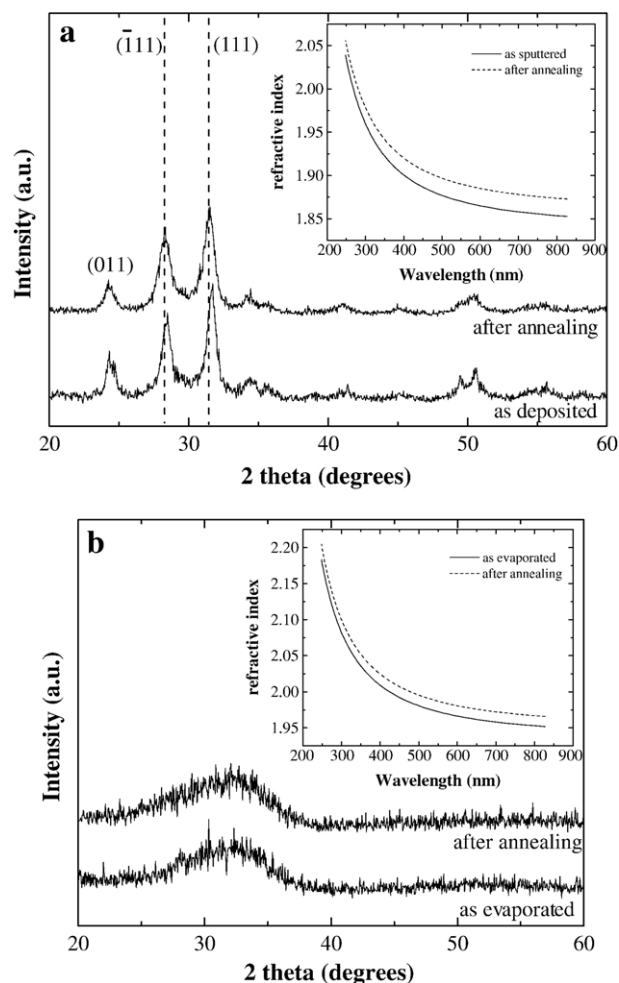


Fig. 1. XRD patterns of HfO_2 samples before and after annealing at 200 °C for 2 h in Ar atmosphere: (a) sputtered films, presenting a nanocrystalline structure when deposited at room temperature and (b) evaporated films that are amorphous even after annealing. The insets show the refractive index obtained from SE simulation using a Lorentz oscillator to simulate the optical response of HfO_2 .

mization of the unbiased estimator (χ^2), resulting from the difference between the experimental and simulation results [11]. The simulation results are shown on Table 1 for both sputtered and evaporated films. The first big difference is the detection of an interfacial layer only in the sputtered films even when produced without heating the substrate. The formation of this layer on sputtered films even at low temperatures was also reported elsewhere [12]. Although this is not important when using this dielectric with other semiconductors than silicon (as in the transparent oxides case), it indicates that nanocrystalline HfO_2 is oxygen permeable during sputtering and annealing. Another important point is that its growth is controlled by the inert atmosphere used during annealing since the thickness of the interfacial layer does not increase significantly. The surface roughness determined by ellipsometry is larger on nanocrystalline films, as expected. It is also possible to see that the fitting is much better (lower χ^2) for the amorphous films, since the dispersion model used to simulate the optical behavior of the HfO_2 was developed for amorphous materials. The inserts in Fig. 1a and b show the refractive index obtained from SE

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