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Electrical behaviour of SiO_xN_y thin films and correlation with structural defects

F. Rebib^{a,*}, E. Tomasella^a, S. Aida^b, M. Dubois^a, J. Cellier^a, M. Jacquet^a

^a Laboratoire des Matériaux Inorganiques, UMR CNRS 6002, Université Clermont-Ferrand (Blaise Pascal),

24 Avenue des Landais, 63177 Aubière Cedex, France

^b Laboratoire de Couches Minces et Interfaces, Université Mentouri, route de Ain El Bey, 25000 Constantine, Algeria

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Abstract

Silicon oxynitride thin films were deposited by reactive r.f. sputtering from a silicon target. Different Ar: O_2 : N_2 gas atmospheres were used at fixed power density (3.18 W cm⁻²) and pressure (0.4 Pa) to obtain various film composition. Pt–Si $O_x N_y$ –Pt sandwich type structure was realised for electrical property investigations. The *C*–*V* measurements showed the absence of a Schottky barrier and thus confirmed that Pt electrode provides an ohmic contact. The evolution of the current density showed a decrease of the film conductivity when the oxygen concentration in the films increases. The various layer composition leads to two different conduction mechanisms which were identified as space charge limited current (SCLC) and Poole–Frenkel effect. Finally, the structural defects of the films were studied by EPR analysis and the spin densities were correlated to both the composition and the electrical behaviour of the films. \bigcirc 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Amorphous silicon oxynitride $(a-SiO_xN_y)$ thin films exhibit interesting properties. They are in the focus of material research for the last 20 years with the aim to replace the conventional SiO_2 for gate dielectrics. Also, they are promising insulators in very large-scale integrated circuits, non-volatile memories, metal-insulator-semiconductor and solar cells [1]. The advantages of this material are real because it exhibits excellent breakdown behaviour and lower mechanical stress than silicon nitride. It possesses relatively high dielectric constant which can reach 7.8 in the case of Si_3N_4 [2–4]. The electrical measurements of $a-SiO_xN_y$ could be used to optimize or calibrate the deposition process, but also to determine the conduction mechanism and the presence and concentration of electron traps. The aim of this work is to investigate such properties. For this, SiO_xN_y thin films were deposited by r.f. magnetron sputtering from pure silicon target in various Ar:O₂:N₂ atmospheres. The electrical measurements of these layers have been carried out on samples with Pt–SiO_xN_y–Pt sandwich configuration. *C–V* measurements were used to characterize the electrical contact. The results of the current– voltage characteristics were discussed in relation with the structural change of SiO_xN_y thin films. Rutherford Backscattering Spectroscopy (RBS) allowed to determine the layer composition while Electron Paramagnetic Resonance (EPR) was implemented to underline the nature and density of the defects.

2. Experimental conditions

Silicon oxynitride films were deposited by reactive r.f. magnetron sputtering at a 13.56 MHz frequency using a silicon target and different Ar:O₂:N₂ sputtering atmospheres at fixed power density and total pressure (3.18 W cm⁻² and 0.4 Pa, respectively). For all the deposits, argon content was kept constant at 70% of the total gas flow rate and the ratio $D_{\rm r} = D_{\rm O_2}/(D_{\rm O_2} + D_{\rm N_2})$ was varied from 0.1 to 0.5 (where $D_{\rm O_2}$ and $D_{\rm N_2}$ are the oxygen and nitrogen flow rates, respectively). The composition of the layers was investigated by RBS using

^{*} Corresponding author. Tel.: +33 4 73 40 53 72; fax: +33 4 73 40 71 08. *E-mail address:* farida.rebib@univ-bpclermont.fr (F. Rebib).

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2 MeV alpha particles and a 15 nA current intensity; the experimental spectra were simulated using SIMNRA program. Film thicknesses were measured by profilometry on a Talystep type apparatus. For electrical characterisations, samples with $Pt-SiO_{x}N_{y}-Pt$ sandwich configuration were realised. I-Vmeasurements were performed by operating in a Faraday box and in dark at room temperature (20 °C). The current values were measured using a Keithley 616 digital electrometer and applying a dc voltage in the range of 0–10 V. Before each measure, the electrodes are shortened in order to evacuate the possible stored charges given by a previous polarisation. Capacitance measurements (C-V) were carried out at 1 MHz frequency using a BIO RAD type capacimeter. Electron Paramagnetic Resonance signals were measured using a X band Bruker EMX spectrometer operating at 9.653 GHz. This analysis is described elsewhere [5].

3. Results and discussion

3.1. Composition and capacitance

X-ray diffraction measurements showed that all deposited SiO_xN_y films were amorphous. The silicon concentration in these layers remained almost constant; it only varied between 32 and 34 at.%. On contrary, the oxygen and nitrogen concentrations were correlated to the sputtering gas composition as it can be seen in Fig. 1. When oxygen flow rate is increased to the detriment of the nitrogen one, SiO_xN_y films have a composition varying from one close to silicon nitride (Si_3N_4) to that of silicon oxide (SiO_2) . Considering the previous results, the composition of the SiO_xN_y samples will be subsequently expressed by the atomic ratio c = [O]/([O] + [N]) = x/(x + y).

To investigate the electrical properties of the thin films, it was necessary to precise the nature of the electrical contact. For this purpose, some measurements of capacitance *C* as a function of applied voltage *V* were performed on layers of various compositions *c* and thicknesses *d* while keeping constant the active area contact A ($A = 7.065 \times 10^{-6}$ m²). It is



Fig. 1. Variation of the atomic ratio c = x/(x + y) of the SiO_xN_y deposit (about 350 nm thick) vs. the gas flow rate $D_r = D_{O_2}/(D_{O_2} + D_{N_2})$.



Fig. 2. Variation of the capacitance of SiO_xN_y films as function of the film composition.

clear from Fig. 2 that the capacitance is independent of the applied voltage; it only depends on the stochiometry of the films. Since *C* is independent of *V*, there is not a depletion region at the Pt–SiO_xN_y interface and the contact is therefore ohmic rather than Schottky. So, the overall capacitance is expected to be given by the geometric expression:

$$C = \frac{\varepsilon_{\rm r} \varepsilon_0 A}{d}$$

where ε_r is relative permittivity and ε_0 permittivity of free space. For example, from results obtained for a film possessing a composition c = 0.54 and different thicknesses, a value of $\varepsilon_r = 8$ was found. This value is intermediate between those given in literature for silicon oxide and silicon nitride films, i.e. in 3.3–4.2 range for the oxide [1,6] and in 6–10 range for the nitride [2,7,8].

3.2. Conduction properties

Fig. 3 shows the variation of the electronic current density versus the applied electrical field for SiO_xN_y films of different



Fig. 3. Dependence of the current density on the applied electrical field for SiO_xN_y films of various compositions.

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