Electrical properties of (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ films deposited on a silicon substrate

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Abstract. Direct current conductance in Al/(Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$/silicon structure was studied, the dielectric layers being deposited by the chemical solution deposition method. The measurements were carried out at room temperature and 320, 340 and 360 K. The results correspond to bulk-limited conduction of the Poole-Frenkel type. High voltages and temperature lead to an additional current rise, explained by thermal excitation and tunneling of electrons through the lowered Poole-Frenkel barrier.

1. Introduction

The use of materials with a dielectric constant much higher than that of silicon dioxide allows one to achieve equivalent capacitance in physically thicker dielectric layers. This explains the recent research effort aimed at replacing the conventional SiO$_2$ dielectric with alternative high-$k$ oxides, such as ZrO$_2$, Ta$_2$O$_5$, HfO$_2$, TiO$_2$ etc. A serious problem is their thermal stability on the silicon substrate. One of the approaches consists in forming two-compound oxides, adding other metal oxides to the high-$k$ metal oxides, e.g. Al$_2$O$_3$ to TiO$_2$. The result is an amorphous dielectric film, with high dielectric constant that is thermodynamically stable on the Si substrate [1]. In the work presented, the current-voltage behavior is studied of a metal-insulator-semiconductor (MIS) structure with (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ films deposited on silicon.

2. Experimental

The substrates were polished p–type CZ Si wafers with resistivity of 6-8 Ω.m and <100> orientation. The (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ layers were fabricated using the chemical solution deposition method formerly referred to as the sol-gel technique [2]. They were deposited by spin coating from a sol solution on silicon wafers. The titanium and aluminium sol were prepared separately. Tetraethyltitanate was used for the Ti sol, and aluminium chloride, for the Al sol. The two sols were mixed together in a molar ratio Al:Ti = 1.5:1. After spin-coating the (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ layers were formed using the technological sequence as follows: i) low temperature annealing at 300°C in oxygen ambient for 1 h; ii) high temperature annealing at 750°C in nitrogen ambient for 1 hour. The deposition method requires individual processing of the wafers: the layer is deposited by spin-coating and is subjected to the treatments mentioned. A thicker layer is obtained by running a second deposition after only the low-temperature annealing. The layer's thickness is thus doubled, e.g. 66 nm and 129 nm. The
thickness and refractive index of the films were measured with a laser ellipsometer at wavelength 632.8 nm, the refractive index was 1.6. In a previous study, the optical band gap of such layers was determined as $E_g=3.3$ eV [3]. The chemical composition was investigated by XPS and RBS [3]. The main elements found in the film are Al, Ti and O, the metals being bound to oxygen as oxides. Aluminium was deposited by magnetron sputtering for upper contacts. Dots with varying contact areas $(2.5 \times 10^{-3}, 6.25 \times 10^{-4}, 2.25 \times 10^{-4}$ and $1 \times 10^{-4}$ cm$^2$) were formed using photolithography. Aluminium was also evaporated on the back side of the wafers. Structures with layers of two thicknesses - 66 nm and 129 nm were investigated.

The current-voltage characteristics were measured at room temperature. For better understanding of the leakage mechanism, these characteristics were taken at 320°, 340° and 360 °K. The experimental results were analysed in terms of various possible mechanisms, such as Schottky emission and Poole-Frenkel emission.

3. Results and discussions

The current-voltage characteristics were taken using a computer controlled Keithley 236 Source Measure Unit. The measurements were carried out on all different contact areas. No dependence of the current density on the contact area was observed. This is an indication of the good quality of the films, the lack of macrodefects and flaws and the films’ uniformity over the entire surface the surface.

Figure 1 shows the current-voltage characteristic of two samples (66 and 129 nm thick) with surface area of $1 \times 10^{-4}$ cm$^2$. At low voltages, the current is non-exponential as function of the voltage and is close to ohmic behavior. This can be explained with hopping conduction, the thermal excitation of trapped electrons from one trap site to another dominating the transport in the film. However, the current-voltage characteristics in this region is not temperature dependent (figure 2). This is why another plausible explanation is space charge-limited currents. At higher electric fields, an exponential rise of the current is observed. To determine the physical mechanisms responsible for the conductivity, the dependence of the current on the electric field was compared for two transport mechanisms known to be important for the leakage in insulators: Schottky and Poole-Frenkel emission. They result from the lowering of a Coulomb potential barrier by an applied electric field [4,5]. The Schottky effect is associated with the barrier at the surface of the electrode and the current is electrode-limited. Poole-Frenkel emission is related to barriers in the bulk of a material – donor sites, acceptor sites and traps. Only traps of the donor type, i.e. neutral when filled and positive when empty, can emit electrons in the conduction band because of field induced barrier lowering. The restoring force between the escaping electron and the positive trap is due to a Coulomb interaction and is twice as high for the Poole-Frenkel effect as compared to Schottky emission, because in the former case the
charge is immobile, while in the latter it is due to the mobile image force. This leads to twice as large barrier lowering for Poole-Frenkel effect:

\[ \Delta \phi_{PF} = \left( e^2 E / \pi \varepsilon_0 \right)^{1/2} = \beta_{PF} E^{1/2}, \]  

(1)

where \( \Delta \phi_{PF} \) is the barrier lowering for Poole-Frenkel emission, \( \beta_{PF} \) is the barrier lowering coefficient, \( e \) is the electronic charge, \( E \), the electric field applied, \( \varepsilon_0 \), the permittivity of vacuum and \( \varepsilon \), the relative dielectric constant.

The current-voltage behavior for Poole-Frenkel emission is given by the formula:

\[ J_{PF} = C E \exp\left[ -(\phi_{PF} - \Delta \phi_{PF}) / kT \right], \]

(2)

where \( C \) is a constant. These equations show that the current logarithm of divided by the electric field, as a function of the square root of the electric field, should be a straight line. Assuming no charges in the dielectric, the electric field was determined as \( E=V/d \), where \( d \) is the film thickness.

Figure 3 shows \( \ln(\text{current density}/E) \) as a function of the square root of the electric field for samples with two thickness, 66 nm and 129 nm. It must be noted that lower conductivity is registered for the thinner sample (66 nm). This might be explained by a difference in the layers’ morphology. A columnar structure is observed in the thicker layers, which probably affects the density and type of defect traps determining the conduction mechanism. Figure 3 shows that two regions with different slopes exist for the greater film thickness. The coefficient \( \beta \) can be determined experimentally from the slope of the linear fit of \( \ln(I/E) \) vs \( E^{1/2} \). The result from figure 3 is \( \beta = 4.8 \times 10^{-4} \) eV \( V^{-1/2} \) cm\(^{1/2} \) for the lower slope region and \( 8.6 \times 10^{-4} \) eV \( V^{-1/2} \) cm\(^{1/2} \) for the higher slope. The relative dielectric constant \( \varepsilon \) can be calculated using the values of \( \beta \) and is 2.44 for the lower slope if Poole-Frenkel mechanism is assumed. This value is quite close to the dielectric constant for optical frequencies \([5,6]\), which is the square of the refractive index \( (n=1.6) \), i.e. 2.56. This fact is good indication for the presence of the Poole-Frenkel mechanism.

**Figure 3.** Natural logarithm of the current vs square root of the electric field for films 66 and 129 nm thick.

**Figure 4.** Arrhenius plot of \((\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}\) 129 nm thick for electric field of \( 7 \times 10^5 \) V/cm.

Assuming a Poole-Frenkel conduction mechanism, the natural logarithm of the conductance \( I/E \) was plotted versus \( 1/T \) in order to determine the activation energy (Arrhenius plot). Figure 4 gives the Arrhenius plot for an electric field of \( 7 \times 10^5 \) V/cm. Equation (2) shows that the slope of the linear fit of \( \ln(I/E) \) vs \( 1/T \) is \( (\phi_{PF} - \beta_{PF} E^{1/2})/k \). For a Poole-Frenkel barrier, \( \phi_{PF} = 0.66 \) eV was calculated.

At the high field region, the slope of the linear curve \( I/E \) vs \( E^{1/2} \) changes (figure 3), which corresponds to higher values of \( \beta \). It should be noted that the slope of the sample with thickness 66 nm is higher than that expected from a Poole-Frenkel mechanism. For electric fields higher than
8.1 \times 10^5 \text{ V/cm} the coefficient $\beta$ at room temperature becomes $8.6 \times 10^{-3} \text{ eV V}^{-1/2} \text{ cm}^{1/2}$ for the sample 129 nm thick and $6.5 \times 10^{-4} \text{ eV V}^{-1/2} \text{ cm}^{1/2}$, for the 66 nm thick one.

It must be noted that the slope of $I/E$ curves versus $E^{1/2}$ is temperature dependent. It increases with the temperature, which corresponds to greater experimental values of the coefficient $\beta_{PF}$ (figure 2). The dielectric constants calculated from (1) become anomalously small. Similar results for the Poole-Frenkel coefficients have been reported in [7]. This behavior could be explained by Hill’s classical theory [8], dealing with Poole-Frenkel emission in amorphous materials. It suggests a thermal-field emission, where a charge carrier in the potential well is partly thermally excited and then tunnels through the reduced barrier. Above a critical high field, the probability of charge transfer by tunneling through the reduced barrier is greater than that of emission over the barrier. The probability of reaching an excited state from which tunneling occurs increases when the temperature rises. In quantum mechanical interpretation, the process is well known as phonon-assisted tunneling mechanism. According to M. V. Fischetti et al [9], the oscillation of oxygen ions in metal – O bonds couple very effectively with thermal electrons and hence define the phonon-assisted conduction mechanism.

We suggest that at high fields the leakage current in the $(\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}$ layer is governed by thermal assisted tunneling, which is also a part of the Poole-Frenkel effect [8]. This is why $\ln(I/E^{1/2})$ is linear over more than four orders of magnitude.

4. Conclusion
Measurements made on Al/(Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$/Si structures suggest that the electrical conduction in the dielectric layer is a bulk process of the Poole-Frenkel type. The plot of $\ln I/E$ as a function of the square root of the electric field $E$ exhibits a linear fit with two slopes. The experimental barrier lowering coefficient $\beta$ determined from the lower slope was used for the calculation of the relative dielectric constant. Its value was found to be quite close to the optical dielectric constant of the layers, providing a good support for thermal-field ionization of traps (Poole-Frenkel mechanism). The activation energy determined from the Arrhenius plot at $E = 7 \times 10^5 \text{ V/cm}$ was 0.66 eV. The conduction at higher fields was explained by a transition from electron emission over the top of the reduced barrier to thermal assisted tunneling directly in the conduction band.

Acknowledgments
This study was supported by the Ministry of Education and Science of Republic of Bulgaria under project TN -1504.

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