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ELECTRICAL CHARACTERIZATION OF *MIS* STRUCTURES WITH SOL-GEL TiO_2(La) DIELECTRIC FILMS

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The capacitance-voltage and current-voltage characteristics of MIS structures with sol-gel TiO_2 (180-230 nm) films doped with lanthanum are studied. The dielectric constant of the undoped films is found to be 60.5, whereas for the TiO_2(La) films with a molar ratio of La/Ti = 0.028 it increases up to 93.5. Further increase of the La/Ti molar ratio, however, leads to a decrease of the dielectric constant. The fixed dielectric charge is of the order of 10^{11} cm^{-2} and the trap density at the TiO_2(La)/Si interface is of the order of 10^{12} eV cm^{-2}. Trap-assisted tunneling of electrons in TiO_2 conduction band is established as the transport mechanism.

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1. Introduction

In modern MOS devices, the operation of a SiO_2 gate insulator with a thickness of a few nanometers is accompanied by charge carrier tunneling by direct Fowler-Nordheim emission from Si into the metal or by trap-assisted tunneling into the SiO_2. Trap-assisted tunneling at lower fields generates leakage currents several orders of magnitude larger than direct Fowler-Nordheim tunneling. Therefore, such leakage currents hinder further miniaturization of MOS ICs. This problem can be resolved by replacement of the SiO_2 gate layer with other dielectrics possessing much higher dielectric constants, ε_d. A TiO_2 thin film is very promising since, its dielectric constant is the highest in comparison with those of Ta_2O_5 or Y_2O_3 as candidates for the active gate dielectric. Different technologies have been developed for the deposition of TiO_2 films [1,2]. Among them, the sol-gel method [3] is the most suitable for preparing films with high homogeneity, purity and rigorous doping control. It has been observed [4] that incorporation of lanthanum in TiO_2 increases its dielectric constant. Unfortunately, TiO_2 films have an increased leakage current in comparison with thermally grown SiO_2 layers [1]. Therefore, the establishment of the carrier transport mechanism through the TiO_2 is an indispensable step in the efforts to decrease the leakage current in the TiO_2 gate dielectric.

In this paper we present results from a study of the electrical properties of sol-gel TiO_2 dielectric films doped with lanthanum. The conduction mechanism through the TiO_2 (La) films is also considered.

2. Experimental details

The sol-gel deposition method for the studied TiO_2 films is described in detail elsewhere [3]. Briefly, Si(111) n-type wafers were dip-coated in a titanium alkoxide solution. Some of the oxides were doped with lanthanum, with three different concentrations, during deposition. The molar ratios

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La/Ti in the deposited TiO_2 films were 0.028, 0.1 and 0.22 [3]. These films will be denoted as $TiO_2(La^1)$, $TiO_2(La^2)$ and $TiO_2(La^3)$, respectively. After deposition, the films were dried in air at room temperature for 24 h and then annealed in air at 700 ^oC for 1 h. This thermal treatment transformed the amorphous TiO_2 structure into the high temperature crystalline form of rutile, and resulted in a sufficiently dense film [5]. The thickness of the TiO_2(La) films determined by ellipsometric measurements was in the range 182 – 233 nm.

For the electrical measurements, metal-insulator-silicon (MIS) capacitors were formed by vacuum evaporation of Al dots through a metal mask onto the TiO_2 surface, and of a continuous Al film on the silicon rear side. The capacitance-voltage (C-V) characteristics were measured with a E7-12 type LCR meter, in temperature range 101-290 K, at 1 MHz and with a 25 mV test voltage. The current-voltage (I-V) measurements were carried out in the temperature range 88-291 K.

3. Results and discussion

The C-V characteristics of the MIS structures with the TiO_2 films are presented in Fig. 1. As seen, for the undoped TiO_2 film the C-V curve is steep, which is indicative of a low density of TiO_2-Si interface traps. Small doping concentrations of La in the TiO_2 films resulted in a small shift of the C-V curve toward negative voltages and a slight decrease in its slope. The increase of the La/Ti molar ratio to 0.22 resulted in a considerable shift of the C-V curve toward positive voltages, and a further decrease of its slope.

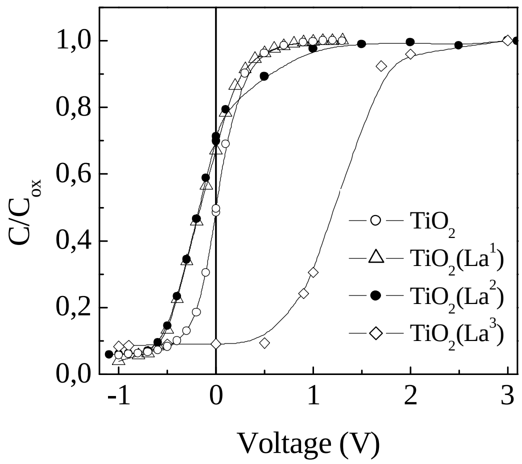

Fig. 1. Normalized C-V characteristics of MIS structures, measured at room temperature.

The values of ε_{ox} were determined from the maximum capacitance C_{ox} ($C_{ox}/S = \varepsilon_{ox}/d$), where S is the Al dot area and ε_{ox} and d are the dielectric constant and film thickness respectively,. For the TiO_2 films, ε_{ox} was 60.5ε_0. For the $TiO_2(La^1)$ film, it increased considerably, to 93.6ε_0. For the $TiO_2(La^2)$ film ε_{ox} was 61.2ε_0, while for $TiO_2(La^3)$ film it was 49.5ε_0. The latter value is even lower than ε_{ox} for the undoped TiO_2. Nevertheless, all these films have ε_{ox} values which are 15 and 25 times higher than that of SiO_2 ($\varepsilon_{SiO2} = 3.8\varepsilon_0$). Since $d_{SiO2} = (\varepsilon_{SiO2}/\varepsilon_{ox})d_{TiO2}$, in order to obtain the same large capacitance changes obtained with Al-TiO_2-Si structures, for a standard Al-SiO_2-Si structure the effective thickness of the SiO_2 layer should be less than 10 nm. Therefore, undesirable effects, such as Fowler-Nordheim tunnelling, as observed through SiO_2, are avoided in the considerably thicker TiO_2 or TiO_2(La) gate dielectric. These results confirm the large potential of sol-gel TiO_2(La) films for application in MOS ICs.

In the flat-band condition, the oxide charge density N_{ox} was calculated from the expression $qN_{ox} = C_{ox}(V_{FB}^i - V_{FB}^e)$, where the V_{FB}^e is the experimental and V_{FB}^i is the ideal flatband voltage. For the TiO_2 films, the N_{ox} value was -1.96×10^{11} cm^{-2} and it increased with the doping level of La. For the $TiO_2(La^3)$ film, its value was the highest ($N_{ox} = -1.2 \times 10^{12}$ cm^{-2}). For the TiO_2-Si and the $TiO_2(La^3)$-Si structures, the sign of N_{ox} was negative, indicating that the oxide charges in these films are connected with trapped electrons. This is in contrast to a SiO_2 gate oxide, where the fixed oxide charge is always positive. At an intermediate doping level, i.e. $TiO_2(La^1)$ and $TiO_2(La^2)$ films, the sign of N_{ox} was positive. The orders of magnitude of the N_{ox} values for our MIS structures were comparable to those of standard SiO_2/Si structures used in contemporary MOS-ICs.

The difference of the V_{FB} values, ΔV_{FB}, of the C-V curves measured at 101 and 290 K is related to the density of electron states, N_{it}, at the oxide-Si interface. The N_{it} values were estimated from the relation $N_{it} = [N_t(T_{m2})-N_t(T_{m1})]/q\Delta V_{FB}$, where T_m is the measurement temperature. The charge captured in the interface traps was positive for the TiO_2-Si and $TiO_2(La^1)$-Si structures and negative in the $TiO_2(La^2)$-Si and $TiO_2(La^3)$-Si structures. This indicates that different types of defect are generated, depending on the doping level of La in the oxide. For all the structures, the N_{it} density was of the order of 10^{12} $eV^{-1}cm^{-2}$, which is comparable to the corresponding values for as-grown SiO_2/Si interfaces in most of the MOS IC.

In order to study the conductivity in the TiO_2(La) films, the I-V characteristics of the MIS structure were measured at different temperatures in the accumulation regime. In this case, the capacitance was maximal and constant, and the applied voltage droped entirely across the film. The forward current characteristics of the undoped and doped with La TiO_2-Si structures were similar, and all considerations and conclusions made from the I-V characteristics of the undoped TiO_2 structures are also valid for the TiO_2(La)-Si structures. For illustration, the forward I-V curves of the TiO_2-Si structures are shown in Fig. 2. As expected, the I-V curves shift towards larger voltages with decreasing temperature. The I-V curves measured at 88 and 107 K practically coincide with each other. For the TiO_2(La)-Si structures, this was observed in the temperature range 90-113 K. This indicates that in these MIS structures, tunneling-type conduction appears at low temperatures. Direct tunneling through the TiO_2 layer (Fowler-Nordheim emission) can be excluded, because the TiO_2 layers are comparatively thick (182 nm). From the analysis of the I-V curves, described in detail elsewhere [6], it was established that the electron conduction mechanism in these structures is inter-trap tunneling.

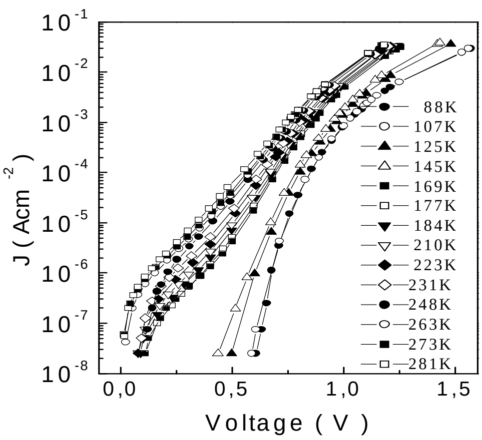

Fig. 2. I-V characteristics of a MIS structure with an undoped TiO_2 film, at different temperatures.

In the case of inter-trap tunneling, charge carriers move from one occupied deep level to the next nearest unoccupied deep level. The current density J for electron tunneling via deep levels at an energy position, $q\varepsilon_t$, close to the quasi-Fermi level in TiO_2 can be expressed [6] as

$$J = \frac{q}{2w^3} w.\nu.\exp[\frac{-2(2m^* q\varepsilon_t)^{1/2} w}{\hbar}].2\sinh[(2m^* q)^{1/2} \frac{w^2 V}{\varepsilon_t^{1/2} d}] \ , \qquad (1)$$

where $1/2w^3$ is the concentration of electrons in deep levels at a distance w from each other and ν is the electron attempt to escape frequency from the traps, of the order of 10^{13} sec^{-1}. Eq. (1) corresponds to a rectangular potential barrier and is valid when Vw/d is considerably smaller than ε_t. Then the slope of a of plot ln(J) vs. V for the forward current at high electrical field is

$$B = \sinh[(2m^* q)^{1/2} \frac{w^2 V}{\varepsilon_t^{1/2} d}] \tag{2}$$

The intersection of the extrapolated plot with the ln(J) axis at V = 0 gives the $\ln J_0$ value, as J_0 is:

$$J_0 = \frac{q\nu}{w^2}.\exp[\frac{-2(2m^* q\varepsilon_t)^{1/2} w}{\hbar}] \tag{3}$$

From the slope B, for the forward current at high electrical fields, and from this $\ln J_0$ value, the energy position $q\varepsilon_t$ of the deep levels and the distance w between them can be calculated. For the TiO_2-Si structures, they were 0.25 V and 3.46-3.48 × 10^{-7} cm, respectively. The density of deep traps N_t in the film can be estimated from the expression $N_t \cong 1/w^3$, giving a value of 2.4 × 10^{19} cm^{-3}. Similar densities of traps, of the order of 10^{19}-10^{20} cm^{-3}, have been observed in Ta_2O_5 films prepared by physical vapor deposition, chemical vapor deposition and anodization of Ta films [7].

Assuming a uniform distribution of the fixed oxide charge N_{ox} in TiO_2, the bulk density of defects N_t can be estimated by dividing N_{ox} by the thickness of the dielectric film, d. In the case of the MIS structure with the undoped TiO_2 film, N_t was 1.08 × 10^{16} cm^{-3}, which differs from the value of 2.4 × 10^{19} cm^{-3} estimated from the tunneling type I-V characteristics. This difference can be explained by the fact that the density of N_{ox} is a result of the superposition of positively and negatively charged defects [8], while N_t is the total defect density of charged and neutral defects.

Since the inter-trap distance w is included in both exponential factors in eq. (1), a minor increase of w will significantly reduce the leakage current through the TiO_2 film. This illustrates the importance of the need to decrease the trap density of TiO_2 films, to open the path for their use as high permittivity gates in future MOS technology.

4. Conclusions

It has been shown that a small amount of La in sol-gel deposited TiO_2 films increases the dielectric constant up to ~ $94\varepsilon_0$. The density of the fixed charge in the films and the density of the traps at the TiO_2(La)-Si interface are comparable to those usually obtained for MOS structures with as-grown SiO_2 gate dielectrics. Analysis of the I-V characteristics of these structures, in the accumulation regime has shown that electron transport in the TiO_2 film occurs by inter-trap tunneling via traps with a density of the order of 10^{19} cm^{-3}. However, the application of TiO_2-Si structures in future MIS devices requires amelioration of the sol-gel deposition conditions, to obtain films with lower trap densities and reduced leakage currents through the TiO_2 dielectric.

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