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Effect of deep levels on the capacitance of MIS structures with sol-gel TiO_2 films♣

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The capacitance-voltage characteristics of MIS structures with un-doped and lanthanum doped TiO_2 dielectric films, prepared by a sol-gel technique, have been measured at different test voltage frequencies from 100 Hz to 100 kHz. The results showed an increase in the capacitance in the accumulation regime and the dielectric constant of TiO_2(La) films with decreasing test voltage frequency. The average bulk energy density of deep levels, responsible for the observed dependences was estimated to be of the order of 10^{16} $cm^{-3}eV^{-1}$.

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1. Introduction

Because of the high dielectric constant of TiO_2, films deposited onto Si substrates have been extensively studied as a possible replacement of the SiO_2 gate dielectric in future ultra-large scale integrated (ULSI) devices and structures. Metal-insulator-silicon (MIS) structures with TiO_2 as the insulator with different film thicknesses have also found applications for various gas sensors [1]. It has been established that the dielectric constant in some TiO_2 MIS structures increases with increasing TiO_2 film thickness [2]. Also, the dielectric constant of TiO_2 strongly depends on the film deposition techniques used, and its value can be varied in a wide range according to application requirements. For example, the dielectric constant measured at 1 kHz is $(100 - 160)\varepsilon_0$, where ε_0 is the vacuum permittivity of $8.854\text{x}10^{-12}$ F/m, for TiO_2 films, prepared by simultaneous Ti electron beam evaporation and oxygen ion implantation [3]. For plasma enhanced chemical vapour deposited TiO_2 films the dielectric constant, measured at 1 MHz, varies from $20\varepsilon_0$ to $80\varepsilon_0$ [2]. Such variations of the dielectric constant can be connected to the presence of structural defects in the films and/or at the TiO_2/Si interface giving deep levels in the TiO_2 and/or Si forbidden band gaps.

The sol-gel method is one of the most widespread deposition techniques. However, there is scarce information about the frequency dispersion of the dielectric constant of sol-gel TiO_2 films. The establishment of a deep level contribution to the dielectric constant value is indispensable for the characterization of gate dielectrics in both high-k and sensor applications of TiO_2 films. The measurement of the capacitance-voltage (C-V) characteristics of MIS structures in a wide frequency range is a straightforward method for revealing the deep level contribution to the frequency dispersion behaviour of the investigated structures.

We have started the studies on the electrical properties of sol-gel TiO_2 films with a view to their possible application as gate-dielectrics in MIS structures. Here we present results on the study of the effect of deep levels on the capacitance of MIS structures with undoped and La doped sol-gel TiO_2 films. The C-V characteristics, measured over a wide range of frequencies, of these MIS structures have been analysed to explain their frequency dispersion behaviour.

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2. Experimental details

The Si(111) n-type wafers were dip-coated in a titanium alkoxide solution [4]. Some of the oxides were doped with lanthanum, which was introduced into the growing film during deposition up to three different concentrations. The proper composition of the solution for the sol-gel process is summarised in Table 1. The atomic ratios of *La/Ti* in the deposited films were 0.028, 0.1 and 0.22 and, below, these TiO_2 films will be denoted as $TiO_2(La^1)$, $TiO_2(La^2)$ and $TiO_2(La^3)$, respectively.

Table 1. Composition of the solution for sol-gel process

Solution composition	Molar Ratio
$C_2H_5OH/Ti(OC_2H_5)_4$	46.80
$H_2O/Ti(OC_2H_5)_4$	2.55
$HNO_3/Ti(OC_2H_5)_4$	0.01
$La^1(NO_3)_36H_2O/Ti(OC_2H_5)_4$	0.01 (La/Ti=0.028)
$La^2(NO_3)_3.6H_2O/Ti(OC_2H_5)_4$	0.02 (La/Ti=0.10)
$La^3(NO_3)_3.6H_2O/Ti(OC_2H_5)_4$	0.045 (La/Ti=0.22)

After deposition, the films were dried in air at room temperature for 24 h and then annealed in air at 700°C for 1 h. This 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 was in the range 182 – 233 nm.

For the electrical measurements, metal-insulator-silicon (MIS) capacitors were formed by vacuum evaporation of Al dots with an area of $4x10^{-3}$ cm^2 through a metal mask on the TiO_2 surface. A continuous Al film was evaporated for the silicon backside contact.

The admittances (conductance and capacitance) as a function of applied voltage of the formed MIS structures were measured in the frequency range 100 Hz - 100 kHz by a digital impedance meter HP 4274. The measured impedance value of $|Z_m|$ and φ_m at a test voltage frequency of ω was transformed to a capacitance C_m and a parallel conductance g_m of the studied structure by Eq. (1).

$$g_m = \frac{\cos(\varphi_m)}{|Z_m|} \quad \text{and} \quad C_m = \frac{-\sin(\varphi_m)}{\omega|Z_m|} \qquad (1)$$

Because of the limited paper length, here we will consider only the frequency dependence of the C-V characteristics; the conductance dependences of the MIS structures will be published separately.

3. Results and discussion

In all C-V characteristics of the MIS structures with undoped and La-doped TiO_2 films, regions of accumulation, depletion and deep inversion are clearly displayed. In the accumulation regime, when the whole applied voltage is dropped on the film, the capacitance value does not depend on the applied electrical field, but changes with the test voltage frequency. This is demonstrated in Figs. 1 and 3-5, where the C-V curves for a pure TiO_2 film (Fig. 1) and doped $TiO_2(La)$ films (Figs. 3-5) measured at different frequencies are given.

In Fig. 1, the frequency dispersion of the C-V characteristics is evident. With increasing frequency, the C-V curves are slightly stretched toward the positive direction along the voltage axis and the film capacitance in accumulation shows a trend to decrease. This is unambiguous evidence that deep levels in the TiO_2 film bulk and/or at the TiO_2/Si interface take part in the capacitance response bas a function of test voltage frequency. Deep levels with charge carrier capture and emission times smaller than the period of the test voltage contribute to the measured capacitance.

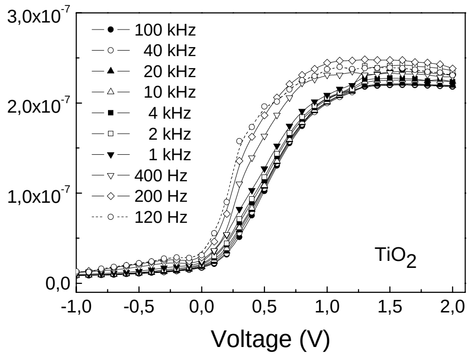

Fig. 1. Frequency dispersion of C-V curves of an MIS structure with a sol-gel undoped TiO_2 film.

The energy density of deep traps responsible for the capacitance changes can be estimated from the difference between the accumulation capacitances measured at different test frequencies [6]. Under a forward bias voltage of 2 V this difference, taken from the 120 Hz and 100 kHz C_m values, is equal to $2.4x10^{-8}$ Fcm^{-2} (Fig. 1). From this capacitance difference, the calculated sheet energy density of deep levels, with response times between 10^{-5} and 10^{-2} s, is equal to $1.5x10^{11}$ cm^{-2}eV^{-1}. These deep levels may be situated either in the TiO_2 film bulk or at the TiO_2/Si interface. If they are in the bulk then the average bulk energy density of deep levels of the sol-gel TiO_2 film, estimated by a division of the sheet energy density by the film thickness, is equal to $8.22x10^{15}$ cm^{-3}eV^{-1}.

The density of the deep levels in the interface region can be estimated from the shift of the C-V curve by the frequency changes under flat band conditions [7]. In the pure TiO_2 films the deep levels at the interface are donor-like and have a relatively small density of $2.75\text{x}10^{11}$ cm^{-2}.

In deep accumulation, the measured capacitance is equal to the film capacitance $C_{max}= \varepsilon_f\varepsilon_0 s/d$, where the contact area *s* and the film thickness *d* are constant. Therefore, the observed change in C_{max} due to the frequency change is due to the frequency dependence of dielectric constant ε_f. This effect can be explained by the presence of deep levels in the MIS structure. As seen in Fig. 2, the dielectric constant, ε_f, of the sol-gel TiO_2 film shows a slight dependence on the measured test voltage frequency in the range 120 Hz - 100 kHz, as ε_f varies between 47.5 and 44.7 with a trend to decrease with increasing frequency. A similar behaviour of the measured capacitance in accumulation and a corresponding change in the dielectric constant of DC magnetron sputtered amorphous TiO_2 are reported in [8]. In this case, the dielectric constant decreases from $22\varepsilon_0$ to $5.5\varepsilon_0$ with increasing frequency from 10 kHz to 1 MHz.

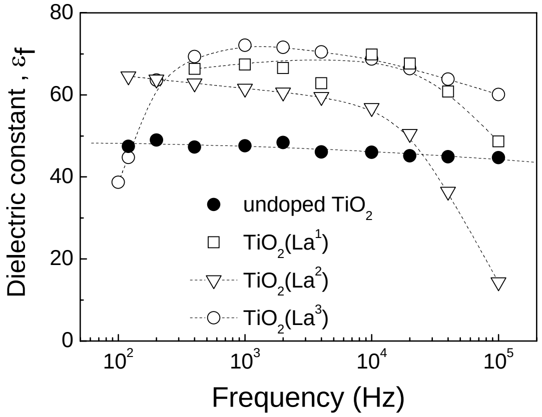

Fig. 2. Frequency dispersion of the dielectric constant, ε_f, of the pure TiO_2 and TiO_2(La) films.

The doped TiO_2(La) films have, in general, higher dielectric constants than undoped ones but their values also exhibit larger frequency dispersions. As is well seen in Figs. 3-5, doping the films with lanthanum leads to a stronger frequency dependence of the capacitance in the accumulation regime. This is also well demonstrated in Fig. 2, where the dielectric constant values of doped TiO_2(La) films, calculated in the deep accumulation regime (2 V), at different frequencies are also given. At the lowest La concentration, the case of the $TiO_2(La^1)$ film, the ε_f value is kept at 68 in a wide frequency range and only above 20 kHz does it fall to 48. Increasing the lanthanum content in the films leads to a more noticeable frequency dependence. At the intermediate La concentration in the $TiO_2(La^2)$ film, as evident in Fig. 4, the frequency dispersion of the capacitance and, correspondingly, the dielectric constant is most pronounced. At frequencies above $2\text{x}10^4$ Hz, the ε_f value of the $TiO_2(La^2)$ film becomes even smaller than that for the pure TiO_2 film. Another special feature of these MIS structures is the highest concentration of deep levels in the sol-gel $TiO_2(La^2)$ film. From the capacitance difference at 120 Hz and 100 kHz, the calculated sheet energy density of deep levels is $1.44\text{x}10^{12}$ $cm^{-2}eV^{-1}$. The corresponding average bulk energy density of these deep levels is $7.3\text{x}10^{16}$ $cm^{-3}eV^{-1}$.

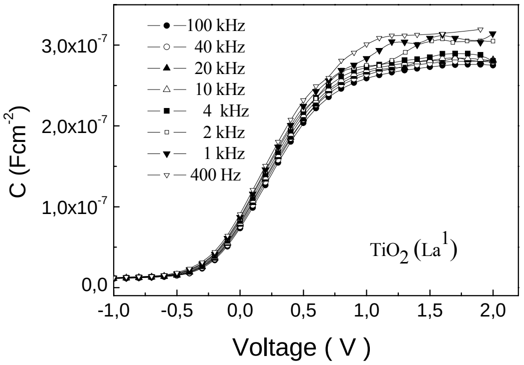

Fig. 3. Frequency dispersion of C-V curves of an MIS structure with a La doped $TiO_2(La^1)$ film.

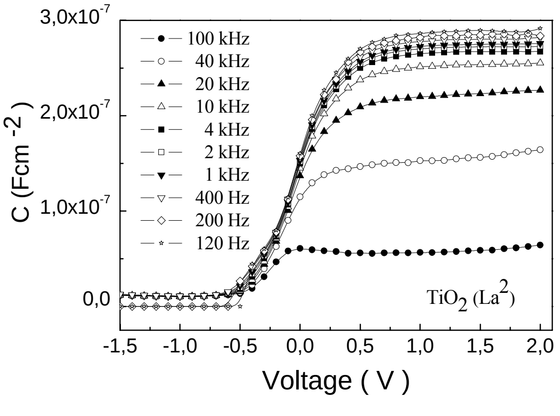

Fig. 4. Frequency dispersion of C-V curves of an MIS structure with a La doped $TiO_2(La^2)$ film.

For the highest doping of La, the case of $TiO_2(La^3)$ films, in the inversion regime a bump appears on the C-V curves, the height of which increases with decreasing test voltage frequency (Fig. 5). The presence of this feature is an indication that there should be a corresponding bump in the density of surface states situated close to the valence band edge of Si. The response time of these states is rather long, of the order of $5x10^{-3}$ s, which is not characteristic of true fast interface states at the TiO_2/Si interface, but of slow interface states in the TiO_2 film nearby the boundary with the Si substrate. Similar bumps have been observed in the inversion regions of C-V curves, measured at 100 kHz, of both p-Si/HfO_2 and n-Si/HfO_2 structures [9] and they have been also connected with interface states. For our MIS structures with the $TiO_2(La^3)$ film, the energy density of deep levels, estimated from the maximum value registered at 200 Hz, of this bump is $4.6x10^{11}$ $cm^{-2}eV^{-1}$. From these results, it follows that when investigating MIS structures the role of deep levels should be taken into consideration not only in the accumulation region but also in the inversion region.

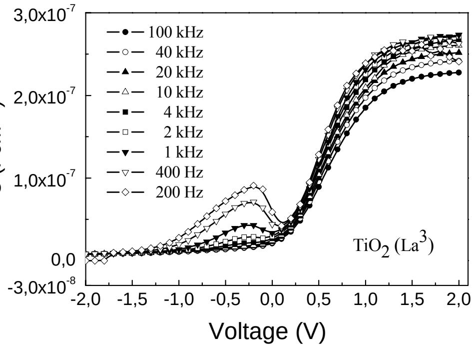

Fig. 5. Frequency dispersion of C-V curves of an MIS structure with a La doped $TiO_2(La^3)$ film.

It is worth noting that for the MIS structures with La doped TiO_2 films, the stretching of the C-V curves by the frequency is smaller (see Figs. 3-5). This is an indication that at the interface the density of deep levels, possessing smaller charge carrier capture and emission times than the test voltage period, decreases to $6\text{-}8x10^{10}$ cm^{-2}.

4. Conclusions

The frequency dispersion behaviour of MIS structures formed with sol-gel TiO_2 films, doped with lanthanum with different concentrations, have been studied. The results have shown that an enhancement of the dielectric constant can be achieved by introduction of La in the films with the atomic ratios of La/Ti being 0.028, 0.1 and 0.22. A clear dependence of the capacitance of these MIS structures on the test voltage frequency has been detected, which is more pronounced in the films doped with La. For all TiO_2(La) films (La/Ti = 0 - 0.22) the dielectric constant decreases with increasing test voltage frequency. This is unquestionable evidence of the contribution of deep levels in these MIS structures to the variation of the dielectric constant of sol-gel TiO_2 films. The estimated average bulk energy density of deep levels in the undoped TiO_2 films is of the order of 10^{15} $cm^{-3}eV^{-1}$ and its value increases to about 10^{16} $cm^{-3}eV^{-1}$ with La doping. In contrast, the density of deep levels, being of the order of 10^{11} $cm^{-2}eV^{-1}$ at the TiO_2/Si interface, decreases 3-4 times upon La doping.

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