Research Article

Electrical Characterization of Sol-Gel Derived TiO_2 Film on c-Si Substrate by Admittance Measurement

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Transport and storage properties of sol-gel synthesized, namely, dip coating technique, titanium dioxide (TiO_2) thin film over crystalline silicon (c-Si), has been investigated by means of current-voltage (I-V) and admittance analysis within different ambient. Considering the work function of anatase TiO_2 film, determined by both FTIR and TG/DTA analysis, silver (Ag) as front metal electrode was chosen to hinder a barrier for charge carriers. Electrical analysis implied that $\text{Ag}/\text{TiO}_2/\text{c-Si}$ structure was actually constituted by $\text{Ag}/\text{TiO}_2/\text{native silicon dioxide (SiO}_2)/\text{c-Si}$ [SIS] structure, in which SiO_2 layer was identified by FTIR analysis. Consequently, the electrical features of the film were interpreted in terms of SIS diode that is capable of explaining C-V features.

1. Introduction

Titanium dioxide (TiO_2) film deposited on silicon substrate (c-Si) has been extensively studied for the purpose of replacement of SiO_2 gate dielectric films in the future ULSI devices because of its high dielectric constant. Energy band gap of TiO_2 is around 3.5 eV and its dielectric constant lies in between 40 and 110 while SiO_2 film has 9 eV with dielectric constant as 4. Depending on the growth process, TiO_2 film anatase and rutile phases. The rutile phase is thermally more stable and higher dielectric constant compared to anatase phase. Phase transition takes place from anatase to rutile under heat treatment above 700°C [1].

Apart from high dielectric constant and resistivity, TiO_2 films demonstrate low density of surface states and high optical transparency over a wide spectral range with high refractive index as optical properties [2]. Therefore, TiO_2 thin films have several applications like insulator and protective layers in electronic devices and antireflective layers for optical coatings and so forth [2].

TiO_2 thin films could be grown by several methods such as sputtering [3], e-beam evaporation [4], chemical vapor deposition [5], pulsed laser reactive evaporation [6], and sol-gel methods [7]. Apart from them, the advantages of

sol-gel method are being cheap and an easy way to control the optical and the other features. Recent study on organic light emitting diode (OLED) shows that TiO_2 films serve as electron injecting material due to their n-type semiconductor behavior. Within this respect, its electrical properties should be clarified due to lack of information in the literature. Moreover, presence of Si-O bond proposed a formation of a native insulator in between TiO_2 film and silicon substrate, turning the $\text{TiO}_2/\text{c-Si}$ structure into $\text{TiO}_2/\text{SiO}_2/\text{c-Si}$ diode, namely, semiconductor-insulator-semiconductor (SIS) diode. Consequently, the electrical properties of the TiO_2 film were analyzed for the first time in terms of SIS structures in this work.

2. Experimental

2.1. Synthesis of Sol. At first, 4 mL titanium tetraisopropoxide [$\text{Ti}(\text{OC}_3\text{H}_7)_4$] was added in 42 mL ethanol ($\text{C}_2\text{H}_6\text{O}$) and the solution was stirred for 1 hour with a magnetic stirrer to prepare a TiO_2 solution. Afterwards, 10 mL glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) and 28 mL ethanol were added in the solution and stirred for an hour. Finally, 4.5 mL triethylamine [$(\text{S}_2\text{H}_5)_3\text{N}$] was added and the solution was stirred 3 hour. The sol was left to dry in open atmosphere for TG/DTA analysis.

FIGURE 1: (a) TG/DTA measurement curves on TiO₂ sol and (b) UV-transmittance measurement of TiO₂ film grown on glass. The inset shows Tauc plot to determine the band gap of the present film.

For optical properties, the sol was deposited on soda lime glasses (SLG) by dip coating and dried at 150°C for 20 min. Then, postannealing was performed at 200°C for an hour. For electrical analysis, c-Si substrate with 1–3 Ω cm resistivity and 400 μ m thickness was chemically clean through RCA cleaning procedure. A double layer TiO₂ film was coated on Si wafer by dip coating. After each layer, the structure was dried at 150°C for 20 min. At the end, the structure was postannealed at 500°C for an hour and then Ag metal was deposited as a front metal forming Ag/TiO₂/p-c-Si structure.

2.2. Measuring Tools. The sol was allowed to dry in open atmosphere at room temperature and powder was used for TG/DTA, performed with Seiko SII Exstar 6000 TG/DTA 6300 model using an Al₂O₃ crucible in static air ambient with a heating rate of 10°C/min.

The optical properties of the film were examined by transmittance measurement using PG Instruments T80 model UV-VIS spectrophotometer, on transparent substrate. The structural properties of the TiO₂ film deposited on c-Si have been investigated by Fourier transform infrared (FTIR) spectroscopy using Bruker Tensor 27 model IR spectrophotometer. Additionally, the electrical properties were found out by current-voltage (I-V) and admittance via Keithley 6517A multimeter and HP 4192A LCR meter, at room temperature. The dc properties were analyzed within dark and light ambient with halogen lamp and monochromatic light source whereas in finding the ac features, the excitation signal frequency ($\omega = 2\pi f$) was varied between 1 and 1000 kHz under dark and light ambient.

3. Results and Discussions

TG/DTA curves of the TiO₂ powder (depicted in Figure 1(a)) showed two mass losses that were associated with endothermic and exothermic events. The first endothermic event took place around 90°C denoting elimination of water while exothermic events were due to the volatilization and combustion of CH₃OH, (CH₃)₂CHOH, and CH₃COOH species. The two peaks in the DTA curve appeared at 367°C and 510°C respectively, corresponded to the crystallization of the amorphous into anatase phase. Above 600°C, the anatase-rutile phase transition occurred since there was no mass loss in TG curve.

To approve the phase of the structure, the optical transitions were investigated by UV-Vis Spectrophotometry and displayed in Figure 1(b). From indirect allowed transition, energy band gap of TiO₂ film was determined as 3.2 eV and illustrated in the inset of Figure 1(b). This value confirmed the anatase phase of TiO₂ film. On the other side, deconvoluted IR spectra of TiO₂ film on c-Si were shown in Figure 2. The peaks at 478 cm⁻¹ and 584 cm⁻¹ were attributed to Ti–O–Ti and Ti–O polymeric chains. Vibration of the Ti–O–O bond was identified from the bond at 695 cm⁻¹. Moreover, the bonds at 1010 and 1116 cm⁻¹ were ascribed to stretching of Ti–O–C. Furthermore, the bonds at 383, 643, and 748 cm⁻¹ designated the anatase phase of TiO₂ film while the bond at 799 cm⁻¹ denoted for rutile phase of the film. The vibration between 1200 and 1500 cm⁻¹ were due to C–O–H bond. Remarkably, the modes appearing at 1065 cm⁻¹ and 1162 cm⁻¹ were ascribed to symmetric/antisymmetric vibration of Si–O bond, respectively [8]. Lastly the bond at 438 cm⁻¹ might be due to the rocking mode of Si–O bond.

FIGURE 2: Raw (denoted as symbol) and deconvoluted (designated as lines) FTIR spectra of TiO_2 film, deposited on c-Si substrate.

Observation of Si-O bonds in FTIR spectra strengthens the proposition of an existence of SiO_2 native oxide layer in between TiO_2 film and Si substrate, turning the $\text{TiO}_2/\text{c-Si}$ structure into $\text{TiO}_2/\text{SiO}_2/\text{c-Si}$ structure. Consequently, electrical properties of the film were considered in terms of semiconductor-insulator-semiconductor (SIS) diode.

Figure 3 displayed the dark/light I-V curves in forward/reverse direction. As clearly seen, the structure displayed diode property with rectification ratio around 10^4 at $\pm 1\text{V}$. Additionally, the structure showed light sensitive feature where short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were determined as 10^{-7} A and 0.22 V , respectively. Energy band gap of 3.2 eV for indirect allowed transition of TiO_2 film implies the anatase phase. Also, TG/DTA and FTIR analysis confirmed the anatase phase with the characteristic bonds at $383, 643, \text{ and } 748\text{ cm}^{-1}$. On the other side, the work function between silver (Ag) and TiO_2 film revealed a carrier injecting type rather than Schottky. Therefore, diode property was not due to the junction between metal and TiO_2 film. Rather, the junction should be located between the TiO_2 film and Si substrate. Additionally, as shown in Figure 4, $1/C^2$ - V_G curve at 1 MHz indicated two junctions (depletion regions). From the slope, doping of c-Si was verified as 10^{16} cm^{-3} and consistent with $1\text{--}3\ \Omega\text{cm}$ Si substrate [9]. Therefore, carrier concentration of TiO_2 film was calculated as 10^{12} cm^{-3} . Furthermore, the two depleting layers revealed the formation of two junctions in between $\text{TiO}_2/\text{SiO}_2$ and SiO_2/Si . Consequently, the structure turned into semiconductor-insulator-semiconductor [SIS] and admittance measurement would be interpreted in terms of SIS diode.

Generally, the structure of SIS device was comprised of two semiconductors: either as n-i-n or p-i-p where

FIGURE 3: Current-voltage variation of $\text{Ag/TiO}_2/\text{p-c-Si}$ structure under dark/light condition in forward/reverse direction.

FIGURE 4: Dark $1/C^2$ - V_G curve of $\text{Ag/TiO}_2/\text{p-c-Si}$ at 1 MHz frequency.

p and n refer to the doping type of the same or different semiconductors having different (or the same) doping (resistivity) concentrations. For instance, in case of p-type silicon semiconductors, one Si is depleted or inverted and that of the other was accumulated under negative bias. For positive bias, the first one (depleted or inverted one) was accumulated while the other becomes depleted or inverted.

FIGURE 5: (a) Capacitance and (b) conductance as a function of bias voltage on Ag/TiO₂/p-c-Si structure under exposure light.

The similar discussion was also valid for n-i-n type except the bias polarity (opposite polarity).

In the case of differently doped semiconductors, let us say n-i-p, both semiconductors, were depleted or inverted under positive bias while accumulated under negative bias [10]. Depending on the doping concentration of semiconductor, the one with lower concentration was depleted first and that of the higher one becomes depleted at higher positive bias. In case of equal doping concentrations, both surfaces were depleted or inverted simultaneously. For the p-i-n structure, the argument was still valid with opposite polarity.

The influence of surface states on SIS diode was similar to that of MOS device. Under the application of superimposed bias (dc + small signal ac), the semiconductor Fermi level of the insulator-semiconductor interface was swept through the energy band gap of the semiconductor. The response of interface states in the midgap energy region to the excitation signal was such that a conductance (G/ω) peak due to these states would be obtained in the G/ω -V characteristics. With the two insulator-semiconductor interfaces and two sets of interface states, the SIS device displayed two conductance peaks in G/ω -V measurement and two corresponding steps in C-V measurement, respectively. Admittance as a function of bias voltage variations on TiO₂ film grown over p-c-Si was illustrated in Figures 5 and 6. Keep in mind that bias was applied to the metal side to the structure. Considering the TiO₂ as n-type doped, the structure seemed to be n(TiO₂)-i(SiO₂)-p(Si) diode. Also note that due to huge bandgap

differences of TiO₂ (3.2 eV) and Si (1.1 eV) semiconductors, carrier concentration of TiO₂ film was lower than Si semiconductor and illustrated in Figure 4.

In C-V curves (Figure 5(a)) under different light intensities, TiO₂ with $\sim 10^{12} \text{ cm}^{-3}$ was depleted for the bias lying in between -5 and 0 V while the higher c-Si semiconductor depleted at higher positive bias, specifically in the range of 2-7 V. Remarkably, G/ω peaks moved with bias voltage (see Figure 5(b)). The first peak was located around -1 V while the other one manifested itself above 3 V. The shift in G/ω peaks indicated presence of interface trap rather than bulk trap. Also, the two peaks confirmed two depletion regions arose within present structure. Within dark ambient, the sharp decay in capacitance (C) after a maximum in the curve (shown in Figure 6(a)) and without peak in G/ω for positive biases (depicted in Figure 6(b)) implied that the scanned frequency was too high to respond and hence inversion was formed. Under exposure of light, these charges can respond to the ac excitation due to the illumination effect since time constant of these charges decreases [9] and causes an increase in conductance and capacitance, respectively.

4. Conclusion

Sol-gel synthesized TiO₂ over p-c-Si was investigated through structural and electrical measurements. Existence of native silicon dioxide layer was determined via FTIR

FIGURE 6: (a) Capacitance and (b) conductance as a function of bias voltage on Ag/TiO₂/p-c-Si structure within dark ambient.

analysis. Consequently, the structure was interpreted in terms of semiconductor-insulator-semiconductor instead of insulator-semiconductor structure. Upon comparison with the ideal SIS diode [Si-SiO₂-Si], the interpretation seemed successful.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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