Low-temperature deposition of ultrathin SiO$_2$ films on Si substrates

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Abstract. We present a detailed investigation of the properties of silicon dioxide deposited at a low temperature. The advantages of this process include its low thermal requirements (about 200 °C), the absence of corrosive by-products and the lack of need of vacuum equipment. Sol solutions were prepared for the deposition of ultrathin SiO$_2$ films by spin-coating at the low annealing temperature of 200 °C. The layers’ thickness was 24 nm and 5 nm. We describe in detail the material properties of this novel low-temperature SiO$_2$ layers obtained by extensive characterization using Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), XPS spectroscopy, capacitance-voltage ($C-V$) and current-voltage ($I-V$) measurements. The ultrathin oxide layers on Si substrates show good dielectric properties.

1. Introduction

Silicon oxide is widely used for optical and electronic applications. SiO$_2$ of the highest quality can be formed by thermal oxidation of Si at temperatures over 800 °C in dry O$_2$. Thermal oxide is only grown on Si substrates at high temperatures, which limits its applications, as many of those require SiO$_2$ film deposition on different substrates [1]. SiO$_2$ nanolayers have been produced by plasma oxidation, atomic layer deposition, deposition from sol-solutions and oxidation by wet-chemical methods.

In this work we propose a technological approach consisting of liquid chemical deposition from a sol solution that has the following advantages over other deposition techniques: it is cost effective, no vacuum equipment is needed, control of the film’ coverage and thickness is possible. The preparation procedure is also presented of the sol solutions for ultrathin SiO$_2$ layers of different thickness at 200 °C. Two sets of samples were studied, namely, SiO$_2$ films with thickness of 24 nm and 5 nm. The film morphology was studied by AFM. the FTIR investigation confirmed the formation of SiO$_2$. The chemical analysis was performed by XPS. The dielectric properties of the MOS structures were studied by capacitance-voltage ($C-V$) and current-voltage ($I-V$) measurements.

2. Experimental

The SiO$_2$ layers were prepared by the sol-gel technique using tetraethyl orthosilicate (TEOS) as a precursor. The introduction of glacial acetic acid at the molar ratio TEOS:acetic acid 1:15 caused acetate modification, resulting in an exothermic reaction. Further, the solution was modified by a small amount of water. Acetylacetone acts as a stabilizer, so that it was added in the molar ratio

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TEOS:acetylacetone 1:1. Two solutions were prepared with different molar content of TEOS in order to deposit SiO$_2$ layers of different thickness. The films were obtained by spin coating at 8000 rpm for 30 s on Si substrates, the latter being cleaned beforehand by the RCA procedure, which is a standard one for wafer cleaning involving removal of the organic contaminants, of the oxide layer and of the ionic contamination (for details see [2]). The samples were prepared on Si wafers: (n- and p-type Si) with different surfaces: one side polished and one side etched (p/e) and both sides polished (p/p). The annealing procedure included heating at 200 °C for 30 min.

The AFM studies were conducted on a scanning probe microscope DiMultimode V (Veeco). The FTIR measurements were performed by an IRPrestige-21 Shimadzu FTIR Spectrophotometer. The layers were deposited on Si substrates, with bare Si wafer used as a background. The electrical properties of the layers were studied using MOS structures. The XPS studies were performed by a VG Escalab II system using AlK$_\alpha$ radiation with an energy of 1486.6 eV. The chamber pressure was $10^{-7}$ Pa. The binding energies (BE) were determined utilizing the C1s line (from adventitious carbon) as a reference with an energy of 285.0 eV. The accuracy of the BE measured was ± 0.2 eV. The SiO$_2$ films thickness was determined by ellipsometry, thus preparing two sets of films film with thicknesses of 24 and 5 nm.

3. Results and discussions
AFM images of ultrathin SiO$_2$ films (5 nm thick) are shown in figures 1 and 2. The $R_a$ is the arithmetic mean of the absolute values of the height of the surface profile $Z(x)$, where $Z(x)$ is a function describing the surface profile analyzed in terms of the height ($Z$) and position ($x$) of the sample over the evaluation length $L$. The root-mean-square roughness $R_q$ of a surface is similar to the roughness average, the only difference being the mean squared absolute values of the surface roughness profile. The values obtained for the surface roughness were $R_a = 0.74$ nm and $R_q = 0.94$ nm for $L = 500$ nm and, respectively, $R_a = 0.85$ nm, $R_q = 1.07$ nm for $L = 1000$ nm.

For a Gaussian distribution of asperity height, the statistical theory yields that the ratio of $R_q$ to $R_a$ should be 1.25. Some authors note that the asperity height distribution of most engineering surfaces (tribology) may be approximated by a Gaussian distribution with $R_q/R_a$ values of up to 1.31. For our sample, the values of $R_q/R_a$ using data collected from AFM imaging were 1.26 and 1.27, reasonably close to the value of 1.25 predicted by the theory. This result is significant since it indicates that, at the imaging scale, the asperity height distribution of these surfaces are approximately Gaussian and that the statistical relationships for the surface roughness are applicable. The height of the surface profile can be observed from the section analysis. The spectrum of the profile in one section is illustrated in figure 3. The surface smoothness of the layer is assessed by the parameters $R_p$, $R_v$ and $RT$. The maximum profile peak height ($R_p$) denotes the highest peak around the surface profile with respect to the baseline. Likewise, the maximum profile valley depth ($R_v$) is the measure of the deepest valley across the surface profile analyzed from the baseline. Thus, the maximum height of the profile ($RT$) is defined as the vertical distance between the deepest valley and highest peak: $RT = R_p + R_v$. For the samples studied these parameters were as follows: $R_p = 2.5$ nm, $R_v = 1.2$ nm, and $RT = 3.7$ nm.
The results of the AFM measurements demonstrate that the technique used results in homogeneous layers with good a surface coverage of the silicon substrate. The surface layer roughness was in the order of several nanometers and could only be observed by AFM.

XPS spectroscopy was used for determining if SiO₂ was formed (figure 4). The presence of carbon (C1s peak at 285.0 eV) was only registered on the film surfaces; it disappeared after a short-term sputtering (1 minute).

The binding energy of O1s is 532.8 eV, which corresponds to oxide. The Si2p signal is split in two peaks located at 99.31 eV and 103.5 eV. The first peak at 99.31 eV corresponds to a Si-Si bond; it originates from the Si substrate as the sol-gel film is very thin (5 nm). The second peak at 103.5 eV is Si2p3/2, which is an indication of SiO₂. Thus, the XPS analysis proved that we were able to deposit very thin SiO₂ films at a relatively low temperature.

FTIR spectra of the films are shown on figure 5. The SiO₂ films annealed at 200 °C and 300 °C manifested an absorption band in the range of 3400 – 3800 cm⁻¹ assigned to the OH stretching vibration. The absorption bands due to Si-O-Si stretching, bending and rocking modes were observed at 1070.8 cm⁻¹, 805.6 cm⁻¹ and 480 cm⁻¹ in SiO₂ [3]. The absorption at 670.4 cm⁻¹ can be attributed to Si-Si bonds due to oxygen vacancies [4, 5]. The FTIR spectra reveal that ultrathin SiO₂ films have been formed at these low annealing temperatures. These results are in agreement with the results obtained for low temperature thermal-ALD SiO₂ [6].

The electrical properties of the sol-gel SiO₂ films were investigated by measuring their capacitance-voltage (C-V) and current-voltage (I-V) characteristics. For the capacitance- voltage
measurements we used a probe head with an area of the Hg dot of 3.4×10^{-3} cm^2 and 2×10^{-4} cm^2. The MOS structure samples investigated are presented in Table 1. Figure 6 presents the volt-capacitance characteristics of the two groups of samples.

The dielectric permeability $k$ of sample 5 with thickness 24 nm as determined from the capacitance measurements was 3.89; it was lower for the ultrathin layers (5 nm). The hysteresis of the $C$-$V$ curves was also studied. The measurement started at 0 V, the voltage was then swept to inversion, to accumulation and was looped back. The flat band voltage $V_{\text{fb1}}$ was determined from the first $C$-$V$ curve swept from inversion to accumulation, while $V_{\text{fb2}}$ was determined from the $C$-$V$ curve swept from accumulation to inversion. Using the difference $V_{\text{fb1}} - V_{\text{fb2}}$, the density $N_t$ of the trapped charge was calculated using the formula

$$N_t = \frac{C_{\text{ox}}(V_{\text{fb1}} - V_{\text{fb2}})}{q},$$

where $C_{\text{ox}}$ is the capacitance of the layer per cm^2.

Table 2 presents the results for $N_t$ calculated from the measurements at three points of the samples described in Table 1. For structures with a p-Si substrate, the hysteresis character of the $C$-$V$ curves indicates trapping of holes in the dielectric. In the ultrathin SiO$_2$ layer (sample 15), the trapped charge is positive and 2.4 times greater than that for sample 5. For structures with an n-Si substrate, the hysteresis character of the $C$-$V$ curves indicates trapping of electrons in the dielectric (negative trapped charge). In the ultrathin SiO$_2$ layer (sample 20), the trapped charge is negative and 4 times greater than that for sample 10 ($d = 24$ nm) [7].

The $I$-$V$ measurements were conducted at a negative voltage polarity with respect to the Hg dot for the p-Si substrate, and a positive one for the n-Si substrate, to ensure that the Si substrate is in accumulation mode (avoiding the voltage drop across the depletion layer in the Si substrate). The $I$-$V$ data are presented in figure 7. These characteristics demonstrate the good dielectric properties of the ultrathin SiO$_2$ layers.
Table 2. Estimated results for the trapped charge density $N_t$.

| No | Substrate type | Oxide thickness [nm] | $V_{fb1}$ | $V_{fb2}$ | $V_{fb1} - V_{fb2}$ | $N_t$ [cm$^{-2}$] |
|----|----------------|----------------------|----------|----------|------------------|----------------|
| 5  | p-Si           | 24                   | 0.096    | -1.280   | 1.376            | 3.70E+12       |
| 5  | p-Si           | 24                   | 0.037    | -1.278   | 1.315            | 3.70E+12       |
| 5  | p-Si           | 24                   | 0.006    | -1.217   | 1.223            | 3.29E+12       |
| 10 | n-Si           | 24                   | 0.017    | 0.546    | -0.429           | -1.05E+12      |
| 10 | n-Si           | 24                   | 0.051    | 0.526    | -0.475           | -1.18E+12      |
| 10 | n-Si           | 24                   | 0.128    | 0.501    | -0.374           | -9.87E+11      |
| 15 | p-Si           | 5                    | -0.022   | -1.232   | 1.210            | 8.61E+12       |
| 15 | p-Si           | 5                    | -0.036   | -1.242   | 1.206            | 8.76E+12       |
| 15 | p-Si           | 5                    | 0.170    | -1.160   | 1.330            | 7.96E+12       |
| 20 | n-Si           | 5                    | 0.070    | 0.667    | -0.597           | -4.42E+12      |
| 20 | n-Si           | 5                    | 0.103    | 0.661    | -0.558           | -4.06E+12      |
| 20 | n-Si           | 5                    | 0.107    | 0.665    | -0.558           | -4.03E+12      |

The sign "−" denotes a negative trapped charge, “+”, a positive one.

4. Conclusions
The technological process proposed allows one to successfully deposit ultrathin films (5 and 24 nm) of SiO$_2$ on Si substrates at low temperatures. We present detailed material properties of the SiO$_2$ layers obtained by extensive characterization using FTIR, AFM, XPS spectroscopy, capacitance-voltage (C-V) and current-voltage (I-V) measurements. Thus, we proved that the SiO$_2$ films deposited at low-temperature are uniform, smooth and possess good electrical properties. The results obtained indicate that these films can be applied as tunneling-type layers and passivation layers in advanced solar cells or in optoelectronics.

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