Optical properties of silicon rich silicon oxides obtained by PECVD

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Abstract

In this work optical properties of SiO<sub>X</sub> (0 < X < 2) layers obtained by plasma enhanced chemical vapor deposition are studied. Infrared spectra and refractive index dependences with the reactant gases flow ratio R are explained for as deposited, aged and thermally treated samples in the R range from 9.17 to 110. Variations are found to be influenced mainly by sample stoichiometry, density and Si–OH bonds concentration.

Keywords: Optical properties; Refractive index; Plasma enhanced chemical vapor deposition

1. Introduction

Silicon oxides are widely used in microelectronics as intermetal dielectric layers, passivation layers and lithographic masks [1–3]. They also find applications in integrated optics, where the dependence between the oxide stoichiometry and refractive index make it useful in the construction of waveguides. More recently, the discovery of photoluminescent properties of porous silicon [4] attracted further attention to silicon-based materials, as the dream of obtaining completely silicon-based optoelectronic integrated circuits was getting closer. Silicon nanocrystals embedded in a silicon oxide matrix were also found to exhibit photoluminescent properties [5,6], with the advantage over porous silicon of being mechanically more resistant. Oxide surrounded silicon nanocrystals can be obtained by thermally stimulated segregation of excess silicon in substoichiometric oxides (SiO<sub>X</sub>, 0 < X < 2). Still, post-deposition thermal treatments also affect oxides impurity content and mechanical and optical properties, which directly affect.

Plasma enhanced chemical vapor deposition (PECVD) is a technique widely used for the deposition of silicon oxides [7–9]. SiH<sub>4</sub> and N<sub>2</sub>O are commonly employed reactant gases, and their flow ratio R = [N<sub>2</sub>O]/[SiH<sub>4</sub>] determines the resulting oxide stoichiometry. For this work, PECVD silicon oxides were obtained using SiH<sub>4</sub> and N<sub>2</sub>O as reactant gases and varying R in a wide range. The effects of aging and thermal treatments were investigated following changes in infrared spectra of the oxides.

2. Experimental

PECVD silicon oxide layers were deposited in a large radial flow capacitively coupled parallel-plate PECVD reactor [10], operated at 13.56 MHz. Undiluted SiH<sub>4</sub> and N<sub>2</sub>O were used as precursors. Chamber pressure, r.f. power density, nitrous oxide flow and substrate temperature during depositions were fixed at 26.6 Pa, 0.07 W/cm<sup>2</sup>, 110 sccm and 300 °C, respectively. The reactant gases flow ratio R = [N<sub>2</sub>O]/[SiH<sub>4</sub>] was varied between 9.17 and 110. The films were deposited on one-side polished p-type (14–20 Ohm cm) silicon (100) wafers (50 mm diameter and 240 μm of average thickness). Layers about 1 μm thick similar to those used for integrated optics applications were obtained.

Thickness and refractive indexes of all samples were measured with a Rudolph Research Auto El IV ellipsometer operating at 632.8 nm and 70 °C incidence angle. The samples were subjected to thermal treatment at 300 °C for 1/2 h in ambient atmosphere. Transmission FTIR spectra were obtained with a Perkin–Elmer Model 2000 spectrophotometer, the reference being silicon wafer analogous to the substrates.
3. Results and discussion

Fig. 1 shows representative IR spectra of PECVD oxides. Three main absorption bands are present at around 1070, 800 and 640 cm\(^{-1}\), characteristics of Si–O–Si stretching, bending and rocking vibrations, respectively [11]. Si–O stretching band is the more intense of all and it carries a great amount of information about the oxide. Its vibration frequency depends of Si–O–Si bond angle and near neighbors, thus being influenced by strain/stress, stoichiometry, density, and porosity of the SiO\(_X\) films [12,13]. As we increase \(R\) from 9 to 22, the Si–O stretching band shifts to higher wave numbers and its width decreases (Figs. 1 and 2). This results from the rising oxide stoichiometry while \(R\) grows. Stoichiometry changes are also reflected in the refractive index \(n\), which approach that of the stoichiometric oxide while \(R\) increases to 22 (Table 1). For \(R\) around 22 nearly stoichiometric layers are obtained [14]. The behaviors of \(n\) and of the stretching band position and width in the \(R\) range from 22 to 110 are opposed to those observed in the lower \(R\) range (9.17–22) (Table 1 and Fig. 2). For a material which is no longer changing its composition, a rise in the refractive index means a higher density according to Lorent–Lorentz equation [15]. The higher density might well be a consequence of the lower deposition rates observed for higher \(R\) values (Table 1). The behaviors of \(n\) and the deposition rate with \(R\) made us conclude a rising density as \(R\) grows, implying a lower porosity, i.e. lower area for OH adsorption for maximum \(R\) values. Combined variations of porosity and Si–H bond concentration cause Si–OH bonds concentration to peak in an intermediate \(R\) value (approximately 22) and decrease for extreme \(R\) values.

Aging and thermal treatments at 300°C for 1/2 h produce a blue shift of the Si–O stretching band and a decrease of its width (Fig. 2). The effects are specially marked for \(R\) near 22, additionally signaling this value as a turning point of sample behavior. This is correlated with the dependence of Si–OH bonds concentration with \(R\), which also peaks at \(R = 22\) (Fig. 3) (the concentration was qualitatively estimated from the area of the Si–OH stretching band between 3000 and 3800 cm\(^{-1}\) (Fig. 1)). Si–OH bonds are formed in deposition chamber and by adsorption after exposure to atmosphere (hence the higher concentrations for aged samples (Fig. 3)). Their formation is affected both by Si–H bond concentration and porosity of the samples: Si–H bonds block OH adsorption [16] while porosity directly affects the area exposed to OH adsorption. But it is known that Si–H bonds concentration diminish when \(R\) grows [14]. Besides, the behavior of \(n\) and the deposition rate with \(R\) made us conclude a rising density as \(R\) grows, implying a lower porosity, i.e. lower area for OH adsorption for maximum \(R\) values. Combined variations of porosity and Si–H bond concentration cause Si–OH bonds concentration to peak in an intermediate \(R\) value (approximately 22) and decrease for extreme \(R\) values.

How OH adsorption affects Si–O stretching band position and width is explained considering that absorption occurs in those Si–O–Si bonds that are chemically more reactive, with angles lower than around 120° [17]. These bonds are considered stressed and they absorb at lower frequencies than bonds with angles between 120 and 180°. Hence, OH adsorption must lead to a blue shift of the stretching band. Furthermore, the reduction of Si–O–Si bonds angle distribution must lead to a reduction of the stretching bandwidth. All mentioned effects should be bigger at the maximum OH adsorption \(R\) value (22, Fig. 3), just as observed (Fig. 2).

![Fig. 1. Representative IR spectra of PECVD silicon oxides deposited with different reactant gases flow ratio \([\text{N}_2\text{O}] / [\text{SiH}_4]\).](image)

![Fig. 2. Dependence of Si–O stretching band position (full symbols) and width (empty symbols) on the reactant gases flow ratio for PECVD silicon oxides as-deposited (■, □), three months aged (○, ○) and thermally treated at 300°C for 1/2 h (▲, △).](image)

**Table 1**

<table>
<thead>
<tr>
<th>(R)</th>
<th>Refractive index</th>
<th>Deposition rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.17</td>
<td>1.504</td>
<td>37.2</td>
</tr>
<tr>
<td>15.71</td>
<td>1.469</td>
<td>45.6</td>
</tr>
<tr>
<td>22</td>
<td>1.462</td>
<td>46.2</td>
</tr>
<tr>
<td>55</td>
<td>1.464</td>
<td>26.4</td>
</tr>
<tr>
<td>110</td>
<td>1.481</td>
<td>17.4</td>
</tr>
</tbody>
</table>
Thermal treatments to 300 °C for 1/2 h lead to a further blue shift of the stretching band position and a decrease of its width (Fig. 2). Si–OH bonds concentration is also seen to decrease (Fig. 3). Had the desorption process being the opposite of the adsorption one, the stretching band behavior should have being the reverse. The observed evolution is instead consequent with a partial reordering of the oxide structure accompanying OH desorption, reordering that would lead to a release of stress in smaller angle Si–O–Si bonds present in the oxide or newly formed by re-linking after neighbors OH desorption.

4. Conclusions

The value $R = 22$ marks a point of change for many properties of PECVD silicon oxides (Figs. 2 and 3). For $R$ ranging from 9.17 to 22, increasingly stoichiometric oxides are obtained with refractive indexes approaching that of SiO$_2$ (Table 1). The infrared spectra also evolve toward that of a stoichiometric oxide, with thinner and blue shifted Si–O–Si stretching absorption bands. For $R$ ranging from 22 to 110 no further changes in stoichiometry are expected. Still, the small increase in the refractive index suggest a higher density, hypothesis supported by the decrease in the deposition rates (Table 1). Tightly related to this is the dependence of Si–OH bonds concentration on $R$, with a maximum at $R = 22$. Water adsorption in stressed Si–O–Si bonds acts as a stress releasing mechanism, explaining the behaviors of Si–O stretching band position and width in the higher $R$ range (Fig. 2). Thermal treatments at 300 °C produce partial desorption of adsorbed water and cause changes in the infrared spectra consistent with a release of oxide stress.

References