Stability of Postannealed Silicon Dioxide Electret Thin Films Prepared by Magnetron Sputtering

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The effect of postannealing on surface potential stability was investigated for silicon dioxide (SiO₂) electret thin films with a thickness of 2 to 5 μm. The SiO₂ films were prepared on Al-coated and uncoated Si substrates by r.f. magnetron sputtering using a fused quartz target. Subsequent to the sputter deposition, the SiO₂ films were postannealed in the deposition chamber in order to improve stability for use in a highly humid atmosphere. The obtained surface potential stability was dependent on not only the postannealing conditions but also the deposition conditions. The surface potential of SiO₂ films postannealed in an oxidizing atmosphere at 275 to 350°C for 10 to 60 min was found to be highly stable when tested at a relative humidity of 90% and a temperature of 60°C. In addition, the postannealed SiO₂ films were stable for use in air for a long term at room temperature.

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1. Introduction

Electrets are of interest for use as dosimeters, acoustic transducers and microrelay switches as well as for the electrostatic anchoring of molecules in nanotechnology.¹⁻⁸⁾ In addition, many recent developments involving the use of integrated and miniaturized device structures have required electret thin films prepared on substrates.^{7,8)} At present, organic polymers such as polytetrafluoroethylene (PTFE) and fluoroethylene propylene (FEP) are in practical use in most applications. However, it is very difficult to prepare suitable polymer electret thin films for many applications, because these organic materials with low melting points have difficulty withstanding the high temperature heat treatment processes involved in device fabrication. Recently, inorganic thin-film electret materials such as SiO₂ and Si₃N₄, with high melting points, have been investigated using various preparation methods as an alternative to organic polymers in many applications.⁹⁻¹⁴⁾ We have recently reported that SiO₂ electret thin films prepared by conventional planar r.f. magnetron sputtering exhibited no surface potential decay when tested in air at room temperature for a long term.¹⁵⁾ The sputtered SiO₂ thin films were stable even for use at a high temperature up to 230°C. However, stability, or surface potential decay of the SiO₂ films, was considerably affected by humidity. The decay in air at high relative humidity was significantly accelerated as the temperature was increased. We have recently found that the surface potential stability of sputtered SiO₂ films could be improved by postannealing in an oxidizing atmosphere.¹⁵⁾

In this paper, we describe the effect of the deposition and postannealing conditions on the surface potential decay in air at high relative humidity: SiO₂ electret thin films prepared by r.f. magnetron sputtering and postannealed in an oxidizing atmosphere.

2. Experimental Procedure

SiO₂ thin films with a thickness of 2 to 5 μm were prepared on Al-coated and uncoated Si wafer substrates at a temperature of 250 to 350°C by conventional planar r.f. magnetron sputtering using a fused quartz target: target and substrate surface separation, 40 mm. The sputter deposition was carried out in an Ar + O₂ mixed gas atmosphere at a pressure of 0.26 to 0.8 Pa with an r.f. power of 80 W: O₂ partial pressure varied from 4 to 20%. A typical deposition rate of about 8 nm/min was obtained with an r.f. power of 80 W. The SiO₂ films were annealed in the deposition chamber after the sputter deposition in order to improve stability in a highly humid atmosphere. The postannealing were carried out at a temperature of 250 to 350°C for 10 to 60 min in an oxidizing atmosphere. The oxidizing atmosphere in the deposition chamber was achieved by introducing an Ar + O₂ mixed gas at a flow rate of 20 sccm after completion of the SiO₂ film deposition. As a result, the gas pressure in the chamber gradually increased from 0.26 to about 655 Pa during a 60 min postannealing treatment.

The SiO₂ films were electrically charged by a method utilizing the corona discharge resulting from a wire electrode and a grid electrode in air at room temperature (RT) with an applied voltage of -5.3 kV. The negatively charged surface potential was varied by changing the voltage of the grid electrode as well as the distance between the grid electrode and the film surface. The resulting charged surface potential was dependent on the above charging conditions as well as the SiO₂ film thickness. After being charged, an aging procedure was performed; all charged SiO₂ films were heat-treated for 1 h in air at 150°C in order to stabilize the initial surface potential (V_{IN}) of the charged films prior to testing. However, after being heat-treated, the level of surface potential (or V_{IN}) was also dependent on the surface potential stability or decay of the charged SiO₂ films during the heat treatment. The surface potential stability of SiO₂ electret films in high rela-

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tive humidity was evaluated using either the measured surface potential (V) or the normalized surface potential (V/V_{IN}).

3. Results and Discussion

3.1 Stability of postannealed films

The surface potential of SiO_2 electret films prepared under optimized deposition conditions by r.f. magnetron sputtering was found to exhibit no decay when tested in air at room temperature (RT) for a long term. Nevertheless, the surface potential decay in air at high relative humidity was significantly accelerated as the temperature was increased, as shown in Fig. 1. On the other hand, we have recently found that the surface potential stability of SiO_2 electret films at high relative humidity could be improved by postannealing in an oxidizing atmosphere; *i.e.*, the obtained potential stability was significantly affected by both the deposition conditions and the postannealing conditions of the SiO_2 films. As an example, the potential decay in a highly humid atmosphere is shown in Fig. 2 for SiO_2 films postannealed at a temperature of 350°C for 60 min in an $\text{Ar} + \text{O}_2$ (20%) mixed gas atmosphere; the surface potential decay of as-deposited and postannealed SiO_2 films prepared at an O_2 partial pressure of 4 and 8% can be compared. It should be noted that the surface potential stability in air at a temperature of 60°C and a relative

humidity of 90% was improved by postannealing; it was also dependent on the r.f. magnetron sputtering deposition conditions. It should be noted that this improvement in potential stability was not obtained when the SiO_2 films were moved from the deposition chamber into air before being postannealed. In contrast, it was found that the surface potential stability of postannealed SiO_2 electret films was relatively independent of film thickness in the range of 2 to $5\ \mu\text{m}$, whereas V_{IN} increased as the thickness was increased. Figure 3 shows typical surface potential decay for postannealed electret SiO_2 films prepared with a thickness of 2 and $5\ \mu\text{m}$ and tested at a temperature of 60°C and a relative humidity of 90%.

3.2 Deposition condition dependence of stability

In order to evaluate the surface potential stability of SiO_2 electret films in a highly humid atmosphere, the following surface potential decay tests were conducted in air at a temperature of 60°C and a relative humidity of 90%. Figure 4 shows surface potential decay as a function of O_2 partial pressure for SiO_2 films prepared at a sputter gas pressure of 0.26 Pa and a temperature of 350°C and postannealed at 350°C for 60 min in an $\text{Ar} + \text{O}_2$ (20%) gas atmosphere; the resulting high stability was not significantly affected by an oxygen partial pressure from 4 to 20%.

Figure 5 shows surface potential decay as a function of sputter gas pressure for SiO_2 films prepared in an $\text{Ar} + \text{O}_2$ (8%) sputter gas at 350°C and postannealed at 350°C for

Fig. 1 Decay of normalized surface potential of SiO_2 films tested under various conditions: in air at RT ($\circ$); at 60°C , 90% ($\square$); and at 80°C , 90% ($\triangle$).

Fig. 2 Surface potential decay of as-deposited (open) and postannealed (closed) SiO_2 films prepared at O_2 partial pressures of 4% ($\circ$, $\bullet$) and 8% ($\triangle$, $\blacktriangle$).

Fig. 3 Surface potential decay of postannealed SiO_2 films with a film thickness of 2 ($\square$) and 5 ($\circ$) μm .

Fig. 4 Surface potential decay of postannealed SiO_2 films prepared at a O_2 partial pressure of 4% ($\square$), 8% ($\bullet$) and 20% ($\triangle$).

Fig. 5 Surface potential decay of postannealed SiO₂ films prepared at a sputter gas pressure of 0.26 (○), 0.4 (□) and 0.8 (Δ) Pa.

Fig. 7 Surface potential decay of SiO₂ films postannealed for 10 (□), 30 (Δ) and 60 (○) min.

Fig. 6 Surface potential decay of postannealed SiO₂ films prepared at a deposition temperature of 250°C (▽), 275°C (◆), 300°C (Δ), 325°C (□) and 350°C (●).

Fig. 8 Surface potential decay of SiO₂ films postannealed at a temperature of 250°C (□) and 350°C (○).

60 min in an Ar + O₂ (20%) gas atmosphere. It should be noted that the surface potential stability decreased as the sputter gas pressure was increased. The sputter gas pressure producing the best result was 0.26 Pa, the lowest pressure available for r.f. magnetron sputtering used in this work. Surface potential decay as a function of deposition temperature is shown in Fig. 6 for SiO₂ electret films prepared at a pressure of 0.26 Pa in an Ar + O₂ (8%) sputter gas and postannealed at 350°C for 60 min in an Ar + O₂ (20%) gas atmosphere. The surface potential of SiO₂ films deposited at a temperature of 275 to 350°C was stable; the potential stability is relatively independent of the deposition temperature. However, the decay of the film deposited at 250°C was considerably faster than that of films deposited at temperatures above about 275°C.

3.3 Postannealing condition dependence of stability

Figure 7 shows surface potential decay as a function of postannealing time for SiO₂ films prepared in Ar + O₂ (8%) sputter gas at 350°C and a sputter gas pressure of 0.26 Pa and postannealed at 350°C in an Ar + O₂ (20%) gas atmosphere. The stability of SiO₂ electret films was relatively independent of the postannealing time in the range of 10 to 60 min, whereas the level of surface potential decreased as the postannealing time was increased. Figure 8 shows typical surface potential decay for SiO₂ films prepared in Ar + O₂ (8%) sputter gas at 350°C and a sputter gas pressure of 0.26 Pa and

postannealed at 250 and 350°C for 60 min in an Ar + O₂ (20%) gas atmosphere. It should be noted that the SiO₂ film postannealed at 250°C was unstable when tested in air at a temperature of 60°C and a relative humidity of 90%. The stability was considerably affected by the postannealing temperature; high stability was obtained in postannealed SiO₂ films postannealed in the temperature range of approximately 275 to 350°C.

3.4 Effects of postannealing

As mentioned above, a highly stable surface potential at high relative humidities could be obtained in SiO₂ films prepared by r.f. magnetron sputtering and postannealed in the deposition chamber. However, high stability in air for a long term at RT is also required for practical applications. The surface potential of SiO₂ electret films postannealed under the optimal condition was relatively stable for use in air at RT. The surface potential decay shown in Fig. 9 compares an as-deposited with a postannealed SiO₂ film: postannealing at 350°C for 60 min in an Ar + O₂ (20%) gas atmosphere. It should be noted that postannealing improved the surface potential stability of SiO₂ films in air for a long term not only at RT but also at a relative humidity of 90% and a temperature of 60°C.

In order to clarify the mechanism causing the improvement in surface potential stability, differences in chemical structure

Fig. 9 Decay in normalized surface potential of as-deposited ($\square$) and postannealed ($\circ$) SiO_2 films tested in air at RT.

Fig. 10 Si 2p XPS spectra of as-deposited and postannealed SiO_2 films.

between as-deposited and postannealed SiO_2 films were investigated using x-ray photoelectron spectroscopy (XPS) and Fourier transformation infrared (FTIR) spectroscopy. Figure 10 shows the Si 2p core-level XPS spectra obtained from as-deposited and postannealed SiO_2 films. Both types of film exhibited the same spectrum consisting of a single peak at 104 eV. It is widely accepted that the Si^{4+} chemical state of the Si atom corresponds to the peak at approximately 104 eV: a Si atom bonding to four oxygen atoms, resulting in an average composition ratio of $\text{Si}/\text{O} = 1/2$.

The absorption spectra obtained by FTIR measurements comparing as-deposited (a) and postannealed SiO_2 films (b) are shown in Fig. 11. It should be noted that as-deposited and postannealed SiO_2 films exhibited the same absorption spectrum consisting of three main peaks. The three absorption peaks at approximately 1110, 820 and 450 cm^{-1} are attributed to Si–O stretching, bending and rocking vibrations, respectively.^{16,17} The Si–O stretching band can be roughly disassociated into two distinctive Gaussian peaks at approximately 1070 and 1180 cm^{-1} .^{16,18,19} The broad half-band width of these peaks may suggest SiO_2 composed of Si–O molecules with various bond lengths, *i.e.*, a lot of structural defects.^{18,19} In Fig. 11, it should be noted that the intensity of the absorption peak around 1070 cm^{-1} , resulting from Si–O stretching vibrations, is lower than the absorption peaks reported in most FTIR data. However, the postannealing effect may not be attributable to differences in structural defects between the SiO_2

Fig. 11 Infrared absorption spectra of as-deposited (a) and postannealed (b) SiO_2 films.

films.

4. Conclusions

High surface potential stability at high relative humidity was realized in silicon dioxide (SiO_2) electret thin films prepared by r.f. magnetron sputtering using a fused quartz target. Postannealing was needed to obtain high potential stability in air at a relative humidity of 90%; the potential decay of as-deposited SiO_2 films was significantly accelerated as the temperature was increased from RT. After the SiO_2 films were deposited on Al-coated and uncoated Si substrates at a temperature of 275 to 350°C , the films were postannealed in an oxidizing atmosphere at 275 to 350°C for 10 to 60 min. The obtainable stability was considerably affected by not only the postannealing conditions but also the deposition conditions of the SiO_2 films. However, investigation have not shown any clear differences in the chemical structure of as-deposited and postannealed SiO_2 films. High surface potential stability at a relative humidity of 90% and a temperature of 60°C was obtained for postannealed SiO_2 electret films. In addition, high stability in air for a long term at RT was realized in postannealed SiO_2 electret films.

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