Effects of chemical composition on humidity sensitivity of Al/$BaTiO_3$/Si structure

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Argon-ion-beam sputtering technique has been applied to deposit barium titanate ($BaTiO_3$) films on silicon wafers at room temperature under vacuum, and then Al/$BaTiO_3$/Si structures were fabricated. Results show that the current and capacitance of these devices are sensitive to the change of relative humidity at room temperature, and saturation absorption (response) time as well as humidity sensitivity of the devices depend on the chemical composition of the $BaTiO_3$ films. For higher annealing temperature and longer annealing time, the oxygen composition increases while fixed charge density decreases. These changes result in lower humidity sensitivity and longer response time.© *1995 American Institute of Physics.*

In recent years, the humidity sensitivity of metal oxide ceramics[1–5] has been extensively investigated. With the development of automation technique, the integration of sensing elements has become an important issue. Based on integrated-circuit fabrication technique, Chen *et al.*[6] have used radio-frequency sputtering technique to deposit $BaTiO_3$ films on silicon wafers at 300–500 °C and then formed metal-insulator-semiconductor structures. Their results showed that the current and capacitance of these devices are very sensitive to the change of relative humidity (RH). In our work, an argon-ion-beam sputtering technique was used instead to deposit $BaTiO_3$ films on silicon wafers at room temperature under vacuum, and then annealing was performed in nitrogen ambient for various temperatures and times. Al/$BaTiO_3$/Si structures thus fabricated were characterized at various relative humidity. The effects of chemical composition and fixed charge density on the saturation absorption time and the humidity sensitivity of the devices were investigated. The effect of the hydrogen ion on the barrier height is used to explain the dependence of the device current on RH.

⟨100⟩ *n*-type silicon wafers with 5–7 Ω cm resistivity were used in this experiment. The wafers were cleaned by the standard RCA process ($NH_4OH+H_2O_2$, then HCI $+H_2O_2$) and their native oxide was removed by HF dip (H_2O:HF=10:1). Barium titanate film was deposited on the wafer surface in an argon-ion-beam sputtering equipment under a vacuum of 1.33 mPa at room temperature. The purity of the $BaTiO_3$ target is 99.9%. The deposition rate is about 0.195 μm/min, and the resulted film thickness is 2.86 μm. The samples were annealed at 400 to 900 °C for 15 to 60 min in nitrogen. Aluminum was evaporated onto the films, and then Al/$BaTiO_3$/Si structures were formed by photolithographic and etching techniques to give a top electrode area of 1.96×10^{-3} cm^2. Gold was evaporated onto the back surface of the wafers to form an ohmic contact, and after installed in an oven, the samples were annealed at 400 °C for 20 min in nitrogen. The chemical composition of the films were examined by Auger electron spectroscopy (AES), and their fixed charge density and capacitance–voltage (C–V) characteristics were measured with a high-frequency C–V instrument at 1 MHz, while their current–voltage characteristics were measured with positive voltage applied to the Al electrode, both at room temperature. The RH of measurement environment was offered by the vapors of five standard saturation salt solutions.

The maximum capacitance of the Al/$BaTiO_3$/Si structure was found to increase by about 51% when RH increases

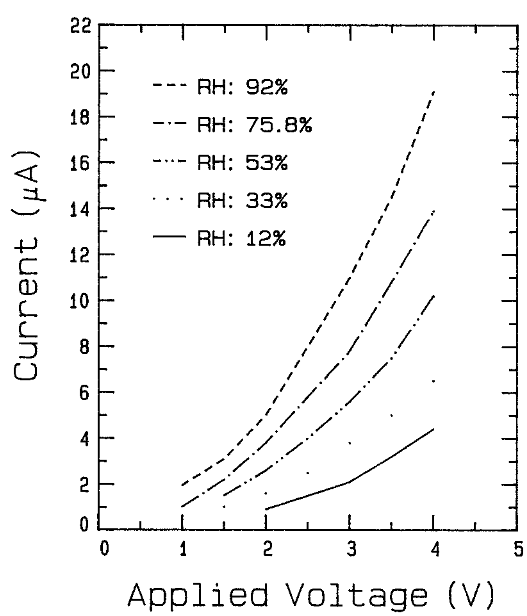

FIG. 1. Dependence of current of Al/$BaTiO_3$/Si structure on relative humidity (room-temperature, samples annealed at 400 °C for 15 min.)

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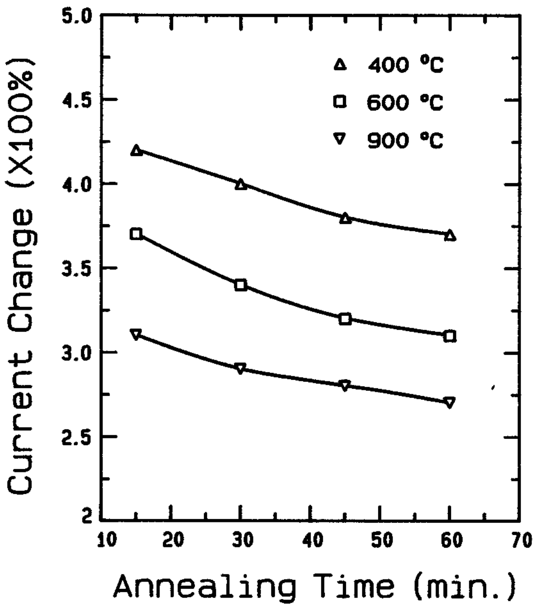

FIG. 2. Dependence of current change of Al/$BaTiO_3$/Si structure on annealing condition (applied voltage = 2.5 V, RH change from 12% to 92%).

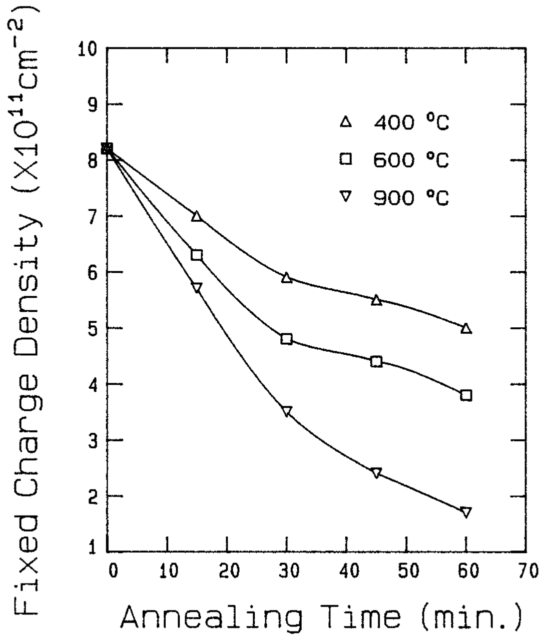

FIG. 4. Influence of annealing condition on fixed charge density of Al/$BaTiO_3$/Si structure.

from 12% to 92%. The change is smaller than others[6] which may be due to the differences in fabrication method. On the other hand, the current of the devices is shown in Fig. 1. At a test voltage of 2.5 V, the current increases by 420% as RH increases from 12% to 92%. The effect of the annealing condition on such a current change of the devices is shown in Fig. 2. The results indicate that the current change induced by the same RH increase gets smaller for higher annealing temperature and longer annealing time. Besides, Fig. 3 depicts that as RH increases from 12% to 92%, the saturation absorption time for water vapor increases with increasing annealing temperature and time.

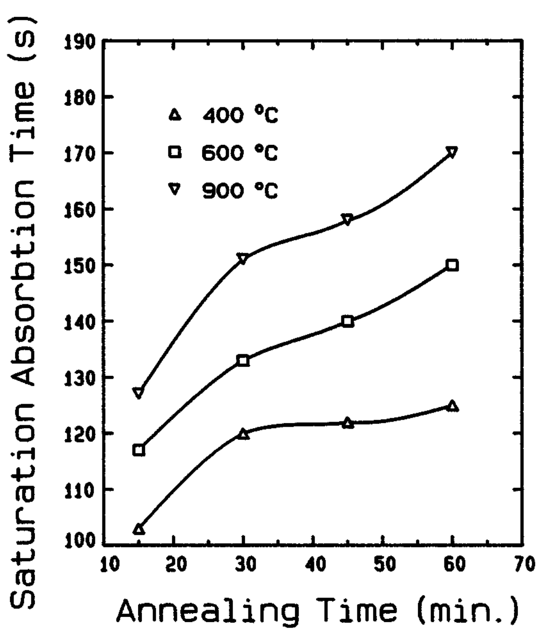

FIG. 3. Influence of annealing condition on saturation absorption time of Al/$BaTiO_3$/Si structure (RH from 12% to 92%).

In order to understand these dependences of the current and saturation absorption time of the devices on annealing condition, the chemical composition of the $BaTiO_3$ films and related fixed charge density Q_f were investigated under a dry environment. Q_f was calculated from the flatband voltage of various samples, and the values are plotted in Fig. 4. It is noted that Q_f decreases with increasing annealing temperature and time. AES shows that the atomic ratio of oxygen in $BaTiO_3$ target is 62%, while it is only 39% in the deposited films before the samples were annealed. Fig. 5 shows the oxygen composition of the samples after different annealing conditions. The oxygen content in the films is higher for

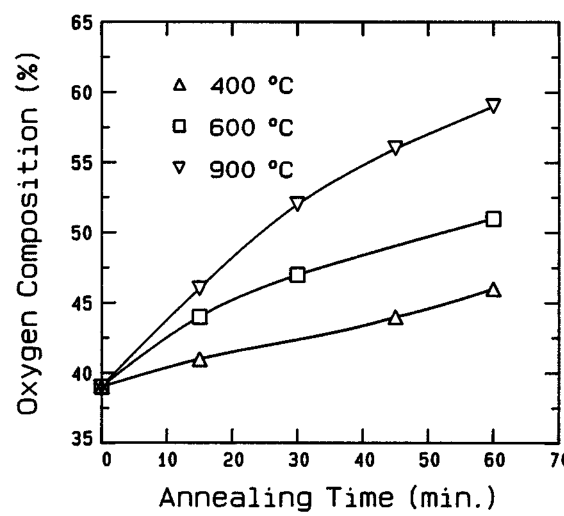

FIG. 5. Oxygen content in $BaTiO_3$ films after various annealing conditions.

higher annealing temperature and longer annealing time. For example, when the samples have been annealed at 900 °C for 60 min, the oxygen composition increases from 39% to 60%. This results in a corresponding decrease of the device current from 8.2 to 4.2 μA (RH = 92%), or from 1.6 to 1.1 μA (RH = 12%).

In this investigation, the increase of oxygen content in this films after annealing is due to the incorporation of the trace oxygen in nitrogen with the dangling bonds in the films, and so Q_f decreases. The longer absorption time for water vapor after annealing at higher temperature or for longer time may be due to the lower Q_f. Since the absorption of water molecules involves both chemisorption and physioroption, and the former is performed by hydroxyl ions reacting with $BaTiO_3$ films, the Q_f decrease in the films is not helpful to the formation of chemisorption layer.

The capacitance increase with RH is due to higher effective dielectric constant of the porous $BaTiO_3$ films after absorption of water vapor. The RH dependence of device current may be explained as follows: at higher RH, the concentrations of H_2O and H^+ in the films increase, and the H^+ ions cause an electric field and potential drops in the films and lead to barrier-height decrease and current increase. The smaller current change after annealing at higher temperature or for longer time may be related to the lower H^+ concentration in the films. This decrease of H^+ ions may be due to the fact that the lower Q_f in the films is not helpful to the decomposition of water molecules. As a note, the crystal structure of the films should have little effect on the humidity sensitivity of our devices because the as-grown films are porous and amorphous, and the annealing temperatures say 400 to 600 °C are too low to cause significant recrystallization in the material.

In conclusion, the electrical characteristics of $Al/BaTiO_3/Si$ structures fabricated by argon-ion-beam sputtering technique are highly sensitive to relative humidity. The oxygen composition in the $BaTiO_3$ films increases with higher annealing temperature and longer annealing time. With higher oxygen composition in the films, the devices exhibit lower fixed charge density, longer saturation absorption (response) time and lower humidity sensitivity.

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