Properties of low-threshold silicon p-MOS capacitors with tin-doped indium oxide (ITO) gates have been investigated. A shift of the capacitance-voltage (C-V) characteristics after annealing the capacitors in an oxygen atmosphere was observed. An anomalous shift of the C-V characteristics is discussed based on the possible presence of negative charge at the ITO-silicon dioxide interface that comes from the diffusion of indium atoms into the silicon dioxide at annealing temperatures above 400°C.

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It is well known that the thermal oxidation of the silicon surface generates a non-mobile positive space charge region within the oxide layer adjacent to the silicon-silicon dioxide interface that has a very substantial effect on the silicon properties at the interface and has severely limited the development of low-threshold p-MOS devices.

In this work we report an anomalous shift of the current-voltage (C-V) characteristics obtained for p-MOS capacitors with transparent conducting ITO gates deposited by sputtering technique with a posterior annealing in oxygen atmosphere. To the extent of our knowledge there is not such report in the literature. Our technological approach allows for obtaining low-threshold p-MOS capacitors that can be useful for different applications.

Experimental

The p-MOS capacitors were fabricated on an n-type 3–5 Ω·cm silicon wafer. The SiO2 layer, with a thickness around 70 nm, was grown at 1000°C. Then, the wafer was cut in two parts for the fabrication of capacitors with aluminum and ITO gates. An Al layer was deposited at the back of both SiO2-Si structures, and on the SiO2 film of the wafer used for capacitors with the Al gate, followed by a short post-annealing in forming gas at 450°C for obtaining an ohmic contact. On the other part of the wafer, the ITO film was deposited on the SiO2 layer by dc magnetron sputtering in pure argon atmosphere, with a power of 100 W, at a 3 mTorr working pressure; we use a ceramic target (AJA International, Inc.) with 90 wt% In2O3 and 10 wt% of SnO2. Fused silica substrates were also used during the same deposition process together with the SiO2-Si structures for optical measurements. A photolithography process was applied for etching the Al and ITO layers in order to obtain the MOS capacitors with a gate area of 2 × 3 mm2. The half wafer containing the ITO-SiO2-Si capacitors was divided in several parts, which together with the ITO films on fused silica substrates, were subjected to a post-annealing process in oxygen atmosphere, at different temperatures (from 200 to 450°C), and for 1 hour at atmosphere pressure.

Results

The electrical and optical properties of the ITO films after the post-annealing in oxygen are summarized in Table I. As-deposited the ITO films in pure argon atmosphere were amorphous showing a poor transparency that may be due to the composition of the sputtered target, whose black color leads to the conclusion that the target may contain foreign phases as metallic tin, indium and/or blue/black suboxides of tin and indium that can be caused by the reducing atmosphere used during the target fabrication. Considerable improvement of the film properties was observed after the annealing in the oxygen atmosphere. The annealing allows for obtaining transparent stoichiometric ITO films, whose conductivity is determined by the tin atoms as well as the presence of oxygen vacancies. The best combination of these dopants, tin and oxygen vacancies, allows to fabricate highly transparent and conducting polycrystalline ITO films after annealing at temperatures from 250 to 350°C. The measured optical bandgap depends on the carrier concentration due to the well-known Burstein-Moss (BM) effect in degenerated semiconductors.

Discussion

From Figs. 3 and 4, a shift in the C-V characteristics of the ITO-SiO2-Si capacitors, in which the ITO gate is annealed in oxygen at temperatures above 350°C, is clearly visible. We can observe an anomalous shift of the C-V characteristics obtained for the capacitors annealed at 450°C. The first reason for this anomalous shift could be the work function of the ITO annealed in the oxygen atmosphere. The change of the ITO work function after the annealing is estimated by comparing the flatband voltage of the ITO-SiO2-Si capacitors with that of the Al-SiO2-Si capacitors shown in Figure 3. The flatband difference (ΔFB) for the ITO-SiO2-Si capacitors relative to the flatband of the capacitor with Al-gate.

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The shift of the C-V characteristics is discussed based on the possible presence of negative charge at the ITO-silicon dioxide interface that comes from the diffusion of indium atoms into the silicon dioxide at annealing temperatures above 400°C.

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Table I. Electrical and optical properties of the ITO films after a post-annealing in oxygen at different temperatures.

| Annealing temperature (°C) | Integrated transparency (400–700 nm) | Resistivity ($\times 10^{-4}$ $\Omega$cm) | Carrier density ($\times 10^{20}$ cm$^{-3}$) | Hall mobility (cm$^2$V$^{-1}$s$^{-1}$) | Optical bandgap (eV) |
|---------------------------|---------------------------------------|----------------------------------------|-------------------------------------------|----------------------------------------|---------------------|
| As-deposited              | 25                                    |                                        |                                           |                                        |                     |
| 200                       | 70                                    | 9.4                                    | 9.2                                       | 11.5                                   |                     |
| 250                       | 75                                    | 3.0                                    | 16.0                                      | 14.7                                   | 4.4                 |
| 300                       | 79                                    | 2.3                                    | 12.0                                      | 19.0                                   | 4.3                 |
| 350                       | 80                                    | 3.3                                    | 4.0                                       | 24.7                                   | 4.0                 |
| 400                       | 81                                    | 10.0                                   | 1.6                                       | 26.0                                   | 3.95                |
| 450                       | 81                                    | 10.3                                   | 1.3                                       | 28.0                                   | 3.9                 |

Figure 1. Dependence of carrier density and optical bandgap on the annealing temperature in oxygen atmosphere.

The value of the ITO work function would be around 5.5 eV; this value is very doubtful, even though it has been reported for ITO film surfaces that have been subjected to a treatment in oxygen or ozone plasma.6,7

Normally the work function should be in the 4.1–4.8 eV range.8–11 Moreover, a very sharp change of the flatband value in the 400–450 °C temperature range requires further attention.

In this regards, we want to bring up the model of metal-induced negative charge at the ITO/SiO$_2$ interface. At annealing temperatures above 400 °C, the work function is decreasing considerably, approaching the value of 4 eV, which is closer to the value of the intrinsic work function of ITO. However, this value is not consistent with the work function values of ITO films annealed in oxygen or ozone plasma, which are usually around 5 eV.5,6

Figure 2. Relative shift of the optical bandgap ($\Delta$EBM) with respect to the optical bandgap of undoped indium oxide (3.7 eV), as a function of the two-third power of the carrier density for the ITO films annealed at different temperatures (dotted lines). Squares show the value of $\Delta$EBM obtained by Y. Sato et al. for the ITO films with different carrier density.4

Figure 3. Quasi-static C-V characteristics of the p-MOS capacitors with Al gate (a) and with ITO gates annealed at different temperatures: b) 350 °C; c) 400 °C; d) 450 °C.

Figure 4. Dependence of the threshold voltage for capacitors with ITO gates annealed at different temperatures and the flatband difference ($\Delta$FB) for ITO-SiO$_2$-Si capacitors relative to the flatband of the capacitor with Al-gate.
above 350 °C, indium can diffuse into the silicon oxide from the non-stoichiometric amorphous as-deposited ITO film with indium excess. The indium diffusivity into silicon dioxide has been reported to be sufficiently high. Furthermore, an abnormal shift of C-V characteristics has been reported for Au-SiO₂-Si capacitors after applying a low-temperature (up to 400 °C) treatment in nitrogen atmosphere, and that shift was explained as due to diffusion of gold atoms into the silicon dioxide. If trivalent indium atoms replace tetravalent silicon atoms in the basic Si₄O₈ tetrahedron, a negatively charged (InSi₃O₈)⁻ ion can be formed. In the case that two indium atoms occupy the position of silicon atoms in the tetrahedron, a double negatively charged (In₂Si₃O₈)²⁻ ion may be formed. This fixed negative charge at the ITO-SiO₂ interface can balance a positive charge at the SiO₂/Si interface, thus explaining the considerable shift of the C-V characteristics in the capacitors with ITO gates annealed at high temperatures.

Experimental evidence of negative charge in silicon dioxide grown on n-type silicon surfaces rinsed with RCA alkaline solution contaminated with trivalent (as indium) aluminum or iron is reported in. Using the well-known equations for a p-MOS capacitor, the negative charge necessary to obtain a zero threshold voltage for capacitors fabricated on silicon substrates with a donor density of 5 × 10¹⁴ cm⁻² and a fixed positive charge of 5 × 10¹⁰ cm⁻² at the SiO₂/Si interface, needs to be 1.5 × 10¹³ cm⁻². This value agrees with that reported for Fe or Al contaminated SiO₂. Of course, SIMS analysis is mandatory to confirm our hypothesis.

Summary

We report experimental results obtained for silicon p-MOS capacitors with ITO-gates annealed. The post-annealing of silicon p-MOS capacitors with ITO gate at temperatures below 400 °C in oxygen atmosphere leads to a shift of the C-V characteristics which can be explained as due to the shift of the Fermi level in the degenerated semiconductor ITO film. For annealing temperatures above 400 °C, the hypothesis of the presence of negative charge at the ITO-SiO₂ interface built during the annealing of non-stoichiometric as-deposited ITO film is discussed. Our reported results are important for overcoming the influence of the fixed positive charge in silicon dioxide in the development of low-threshold p-MOS devices.

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