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Oxidation of silicon surface with atomic oxygen radical anions*

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The surface oxidation of silicon (Si) wafers by atomic oxygen radical anions (O^- anions) and the preparation of metal–oxide–semiconductor (MOS) capacitors on the O^--oxidized Si substrates have been examined for the first time. The O^- anions are generated from a recently developed O^- storage-emission material of $[Ca_{24}Al_{28}O_{64}]^{4+}\cdot 4O^-$ (C12A7-O^- for short). After it has been irradiated by an O^- anion beam (0.5 μA/cm^2) at 300°C for 1–10 hours, the Si wafer achieves an oxide layer with a thickness ranging from 8 to 32 nm. X-ray photoelectron spectroscopy (XPS) results reveal that the oxide layer is of a mixture of SiO_2, Si_2O_3, and Si_2O distributed in different oxidation depths. The features of the MOS capacitor of <Al electrode/SiO_x/Si> are investigated by measuring capacitance-voltage ($C-V$) and current-voltage ($I-V$) curves. The oxide charge density is about 6.0×10^{11} cm^{-2} derived from the $C-V$ curves. The leakage current density is in the order of 10^{-6} A/cm^2 below 4 MV/cm, obtained from the $I-V$ curves. The O^- anions formed by present method would have potential applications to the oxidation and the surface-modification of materials together with the preparation of semiconductor devices.

Keywords: O^- anions, silicon oxidation, MOS capacitor, electrical properties
PACC: 6180J, 7300, 8160

1. Introduction

One of the most important issues in modern microelectronics is the fabrication of dielectric layers with improved capacitance properties to meet the requirements for the dynamic random access memories. The fabrication of high-quantity SiO_2 layers on the Si substrate[1] and the fabrication of alternative dielectrics with high dielectric constants[2–5] are two very important ways. For the formation of a high-quantity SiO_2 layer with a low interface trap density and a low oxide charge density, conventional thermal oxidation of crystalline Si is considered to be a method superior to the others. However, thermal oxidation processes are operated in high-temperature conditions (900–1200°C) and are not applicable to the devices that have already formed a functional structure. Alterative techniques to thermal oxidation, such as plasma-assisted oxidation,[6] laser-assisted oxidation,[7] and high concentrated ozone oxidation[8] have been studied. Moreover, active oxygen species such as atomic oxygen (O), ozone (O_3), and O^-, would be useful for realizing the oxidation of silicon at relatively low temperatures due to their strong oxidation ability.[8–11]

O^- is a monovalent anion (or monovalent negative ion) through the attachment of an electron to atomic oxygen. At the same time, O^- is also considered as a radical because it has an unpaired electron in its outmost orbit. The conventional methods of generating O^- include attaching a free low-energy electron to atomic oxygen and negative ion/molecule reactions that can occur in the following processes: plasma process, electron impact process, or laser irradiation on molecules in gas phase. O^- anions generated by the above methods are generally accompanied by the formation of other ion species.

A new approach to generating pure and stable O^- anions has been developed by our research group.[12–14] The O^- anions can be emitted from the anionic storage-emission material of $[Ca_{24}Al_{28}O_{64}]^{4+}\cdot 4O^-$ (hereinafter in short for C12A7-O^-). A sustainable O^- anion emission current inten-

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sity at a level of $\mu A/cm^2$ from C12A7-O^- has been observed, which shows that the C12A7-O^- can be used as a good O^- anion storage and emitter.[12] Recently, we have also synthesized the various derivatives of C12A7-O^- such as C12A7-OH^-[15,16] and C12A7-H^-.[17,18] More recently, we have also found that the C12A7-O^- material or the modified ones would be practically used in a one-step synthesis of phenol from benzene,[19] the reduction of NO,[20] the dissociation and oxidation of bio-oil,[21] and the fast inactivation of microorganisms.[22]

In the present study, the oxidation of Si wafers via O^- anions which emit from C12A7-O^- material and the preparation of MOS capacitors by the O^--oxidized Si substrates are examined for the first time. For the oxide layers, the elemental composition is analysed by XPS measurement. The electrical properties of the oxide layers in the MOS capacitor configuration are also examined through the $C-V$ and $I-V$ curves. The perfect properties are found by the measurements, indicating that the O^- anions formed by the present method would have potential applications to the oxidation and the surface-modification of materials together with the preparation of semiconductor devices.

2. Experiment

2.1. Material preparations

The Si substrates were n-type (100) oriented wafers with a resistivity of 5–6 Ω·cm. They were cut into a size of 10×10 mm, cleaned with acetone, then rinsed with ethanol and deionized water, and etched with dilute hydrofluoric acid (HF) to remove the natural oxide layers from their surfaces before being used.

The C12A7-O^- sample was synthesized by the solid-state reactions of $CaCO_3$ and γ-Al_2O_3 (at a molar ratio of $CaCO_3$: γ-Al_2O_3=12 : 7) under a flowing dry oxygen environment. The preparation conditions in this contribution were the same as those in the previous work.[13]

2.2. Si oxidation system setup

The experimental setup for Si oxidation with O^- anions is shown in Fig.1. The setup comprised three main parts: (1) an O^- anions emission chamber, (2) a Si oxidation chamber, and (3) an anionic analysis chamber equipped with an anionic time-of-flight (TOF) mass spectrometer. The O^-emission chamber mainly included a C12A7-O^- sample, an electron supply electrode, an anion extraction electrode, and a Faraday plate (or shutter). The C12A7-O^- sample was heated by a quartz-sealed Fe-Cr alloy heater. A stable O^- anions beam was guaranteed by a simple electrochemistry implantation method with supplying the dry O_2 at a pressure of 5×10^{-2} Pa and the electrons generated by applying a low negative DC voltage of –100 V to an electron-supplying electrode on the backside of the C12A7-O^- material. The emitted anions from the C12A7-O^- surface were extracted by

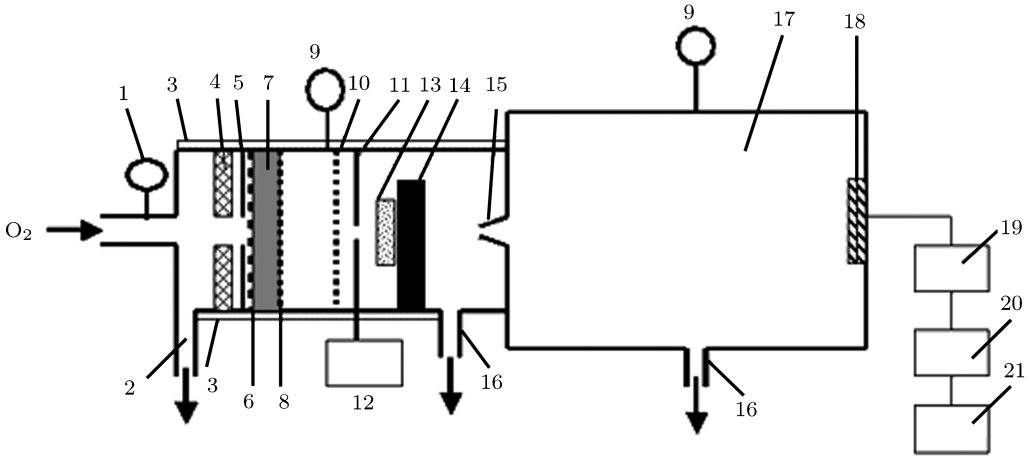


Fig.1. A schematic illustration of Si oxidation using O^- anions. 1: thermocouple gauge, 2: mechanism pump inlet, 3: cooling-water system, 4: heater, 5: quartz plate, 6: electron-supplying electrode, 7: C12A7-O^- sample, 8: anion extraction electrode, 9: ionization gauge, 10: ground electrode, 11: Faraday plate (or shutter), 12: picoammeter, 13: Si wafer, 14: Si sample holder, 15: vacuum skimmer, 16: molecular pump inlet, 17: anion free flight section, 18: tandem micro-channel plates, 19: amplifier, 20: digital oscilloscope, 21: computer-controlled counter system.

an extraction electrode which was supplied by a negative DC voltage of –1000 V. Total emission current was collected by a Faraday plate and detected by a Keithley model 6485 picoammeter. When the process of Si oxidation began, the Faraday plate was replaced with a shutter. Thus, the extracted anion beam passed through the shutter and reached the surface of Si wafer mounted on the sample holder. The gas pressure in the oxidation region in operation was maintained at about 2×10^{-3} Pa. Furthermore, the anions passed through the vacuum skimmer and were analysed by an anionic TOF mass spectrometer.[13]

2.3. Characterization of oxide layer

XPS was used to provide the information about the oxide composition. XPS data were obtained in an ESCALAB-250 apparatus (Thermoelectron Co., USA) with a residual gas pressure better than 1×10^{-9} Pa. Al Kα (1486.6 eV) radiation was used to excite the photoelectrons from the sample. The spectra were obtained under a take-off angle of $\theta = 90^\circ$ (with respect to the surface plane). The energy position of the peaks was determined within an accuracy of 0.1 eV. The photoelectron lines of Si 2p and O 1s were recorded. The binding energies had been corrected with reference to the Si 2p line of the elemental Si at 99.2 eV[23] for all spectra. The peak positions and full-width at half-maximum (FWHM) were determined from the least square fitting using the XPSPEAK 4.1 software. Furthermore, Ar^+ sputtering (1.5 keV, 12 μA/cm^2) was applied to etching the samples for obtaining the composition information from the underlayers. The experimental curves show the recorded data after Shirley background subtraction. It is very important to minimize the adverse effects of the ion beam on the sample stoichiometry during the ion sputtering. It is known that 1–1.5 keV argon ions could sputter conventional SiO_2 keeping its stoichiometric ratio, i.e. the ions remove Si and O at a rate very close to 1:2.[24] Therefore, we assume that a preferential sputtering should not influence considerably the experimental results. The structure of the SiO_2 layer is likely to be damaged during sputtering, but the binding energy of Si 2p or its line width is not affected. For a sputtering time of 0.5–140 min, the thickness reduction measured by XPS was linear with sputtering time.[25]

The thickness of the oxide layers, d, was determined to be more than 4 nm from ellipsometry measurements using a Sopra GES-5 ellipsometer (λ =632.8 nm), and it was less than 4 nm obtained from the XPS measurement with sputtering method mentioned above.

The electrical characterization of the oxide layers was carried out using MOS capacitor with Al gate electrodes of 1.96×10^{-3} cm^2 which were patterned by standard optical lithography. The back of the Si wafer was HF-cleaned followed by Al deposition. The $C-V$ curves were recorded using an Agilent 4294A impedance analyser. The $I-V$ measurements were performed with an Agilent E5270 semiconductor parameter analyser.

3. Results and discussion

3.1. O^- anion beam source

A highly pure and stable O^- anion beam source was developed by using the O^- storage-emission material of C12A7-O^- as an O^- emitter. The emission intensity of the O^- anions was mainly determined by the surface temperature of C12A7-O^- and the extraction field. Figure 2(a) shows a typical mass spectrum emitted from the C12A7-O^- at 800°C and an extraction field of –500 V/cm (the extraction voltage of −1000 V). The dominant peak is for a mass number of 16, which corresponds to O^-. The emission purity of O^-, defined by the ratio of the O^- intensity to total one, was over 95%. To obtain a sustainable and stable O^- emission beam, we adopted a simple electrochemistry implantation method by supplying the O_2 at a pressure of 5×10^{-2} Pa and the electrons generated by applying a low negative DC voltage of −100 V to an electron-supplying electrode on the backside of the C12A7-O^- material at 800°C with an extraction field of – 500 V/cm. As shown in Fig.2(b), the emission current density of O^- anions is stable with a long operating duration by continuously electrochemistry implantation method mentioned above, which allows us to develop a highly pure and stable O^- anion beam for silicon oxidation via the O^- anions. The intensity of the O^- anion beam was controlled by monitoring the sample temperature and/or the extraction field.

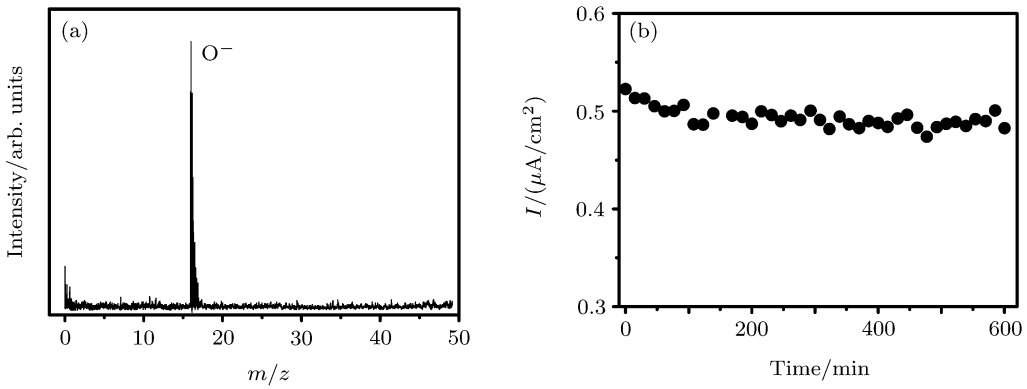


Fig.2. Typical TOF mass spectrum from the C12A7-O^- sample (a), and the emission current density of O^- anions measured as a function of operating time using the electrochemical implantation method (b).

3.2. Si oxidation by O^- anions

The present work provides a method to oxidize or modify the semiconductor materials via the highly pure and stable O^- anions. As illustrated in Fig.3, the oxide thickness (d) on the Si wafers is measured as a function of the running time under the optimal oxidation conditions: O^- anion beam intensity of 0.5 μA/cm^2, Si wafer temperature of 300°C, O_2 pressure of 5×10^{-2} Pa, and the 25 mm gap distance between C12A7-O^- and Si. The thickness of the oxide layer on the Si-substrates is about 8 nm for one hour oxidation, and increases to 32 nm after 10 hour oxidation. The oxidation rate by the O^- anions seems to gradually decrease with the increase of the oxidation layer thickness. According to the constant current oxide growth model,[26] the oxide thickness d can be described as $d = A\ln(1 + Bt)$, where A is the characteristic penetration constant, and B is the initial growth rate of the oxide layer. It is found that the behaviour of the Si-oxidation via the O^- anions accords very well with the prediction from the constant current growth model. The constants A and B are 2.23×10^{-6} cm and 8.35×10^{-5} S^{-1}, respectively. The decrease of oxidation rates with the increase of oxidation time may not result from the diffusion limits or migration effects. Most likely it arises from the anion neutralization in the detachment process ($O^- \rightarrow O + e^-$ and/or $2O^- \rightarrow O_2 + 2e^-$) when the O^- anions pass through the growing oxide layer.

As a comparison, the Si oxidation with dry oxygen (5×10^{-2} Pa) at 300°C was also tested (see Fig.3). The thickness of the oxide layer is neglectable (lower than 1.5 nm) even for 10 hour oxidation via dry oxygen at 300°C, which accords with the previous results that Si oxidation with oxygen does not proceed effectively at temperatures lower than 700°C.[27] The above results show that the O^- anions have a much stronger ability in oxidation than oxygen at low temperatures.

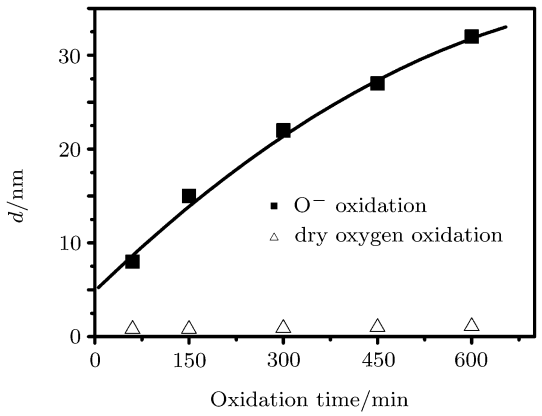


Fig.3. Thickness of oxide layers (d) on Si substrate versus oxidation time.

3.3. XPS analysis

In order to obtain composition information about the O^--induced oxide layers, XPS analysis was performed. Figure 4 presents the variation of the Si 2p spectra of oxide layers (total oxidation depth: 32 nm) in the different depths, in which d_0 denotes the distance from the surface. With the value of d_0 increasing, the peak at binding energy near 103.0 eV becomes weaker and the peaks at binging energy near 99.2 eV turns stronger. Figures 5(a)–5(c) give the simulated XPS results for d_0= 0, 10, and 20 nm respectively. The solid line represents the measured data. At d_0= 0 nm (Fig.5(a)), the spectrum is decomposed into the high binding energy band at near 103.3 eV (referred

to Si_{2p}^{oxide}; FWHM=2.0 eV) which is a typical position of SiO_2 [24] and the low binding energy peak at 99.2 eV (referred to Si_{2p}^{Si}; FWHM=1.4 eV) which originates from the Si substrate. At d_0=10 nm (Fig.5(b)), Si_{2p}^{oxide} band is of a double peak structure and can be deconvolved into two components: SiO_2 (or Si^{4+}) and Si_2O_3 (or Si^{3+}) at 102.4 eV.[24] Thus, Si, stoichiometric SiO_2 and intermediate oxidation state of Si_2O_3 occur in the oxidation layer at 10 nm. Moreover, the Si_{2p}^{oxide} peak shifts toward lower energies with the increase of d_0 (Fig.5(c)). The deconvolution of the Si_{2p}^{oxide} spectrum gives two peaks, which are attributed to the Si_2O_3 and the intermediate oxidation state of Si_2O at 100.2 eV.[24]

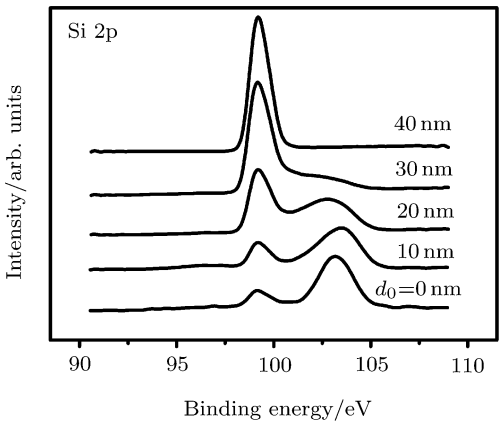


Fig.4. Si 2p spectra (total oxide layer: 32 nm) measured at different values of depth d_0 from the surface.

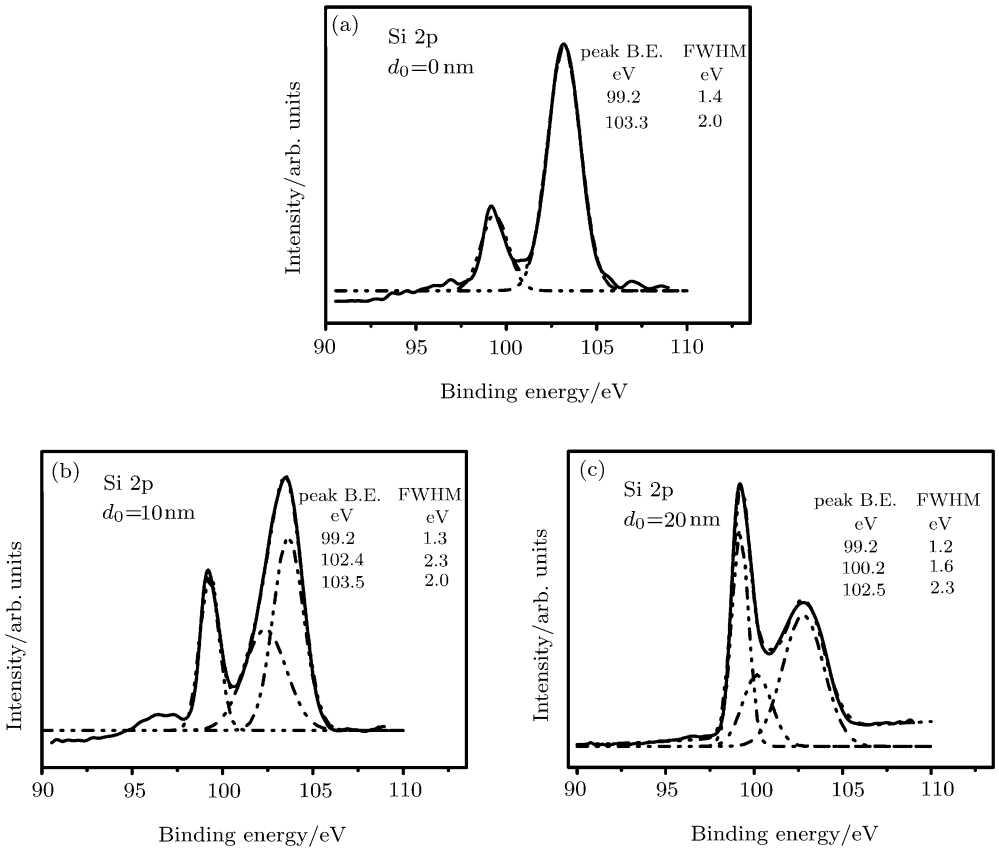


Fig.5. Decomposition of Si 2p spectra (total oxide layer: 32 nm) for different values of d_0: 0 nm (a), 10 nm (b), and 20 nm (c), where "—" denotes as-recorded data, "- - -" represents the decomposition of the components. The corresponding oxidation states are indicated in the panels.

The analyses of the O 1s peaks with different values of d_0 are shown in Fig.6. The O 1s signals were recorded at 533 eV on the surface of the layer, corresponding to the position of SiO_2.[28] With the value of d_0 increasing, the O 1s peaks shift toward lower energies, indicating that the oxidation state of Si is reduced. At the interface between the Si-oxidation layer and Si-substrate, the peak of O1s at 531.5 eV becomes much weak, suggesting that there appears only a small amount of oxide at the interface. XPS results show that the Si oxide formed by O^- anions is nonstoichiometric and nonuniform throughout the oxidation layer. SiO_2 is dominant on the surfaces of the O^--oxidized Si wafers, and the Si_2O_3 and the Si_2O

are dominated close to the interface.

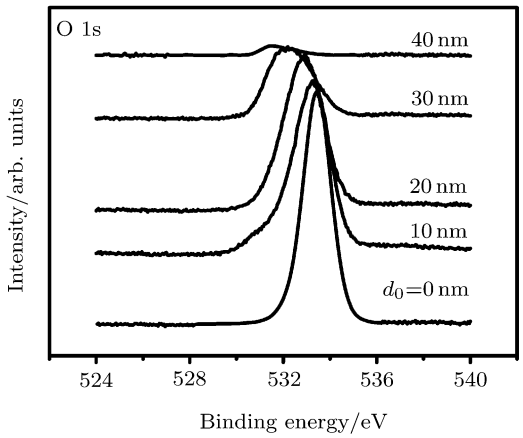


Fig.6. O 1s spectra measured at different values of depth d_0 from the surface with total oxide layer being 32 nm thick.

3.4. Dielectric and electrical properties

In order to examine the dielectric and the electrical properties of the oxide layers formed by the O^- anions, we fabricate the metal-oxide-semiconductor capacitors consisting of <Al electrode/SiO_x film (32 nm)/ Si substrate>. Figure 7(a) shows typical high-frequency *C–V* curves (1 MHz) for the MOS capacitor with an area of 1.96×10^{-3} cm^2. It is observed that the oxide layer exhibits a typical MOS characteristic, represented by regions of accumulation, depletion and inversion. No apparent *C–V* hysteresis is observed when the gate voltage is swept from accumulation to inversion and from inverse to accumulation as indicated by arrows respectively. The flat band voltage (V_{fb}), derived from the *C–V* curve is about –1.6 V. From the flat band voltage, the density of the oxide charge is estimated to be 6.0×10^{11} cm^{-2}, and the difference in work function between Al gate and Si is –0.7 eV. As detected by XPS analysis, suboxides are formed in the oxide layer. The intermediate oxidation state of Si, as well as various microstructural defects behaves as electrically active centres in the form of oxide charges. Furthermore, the capacitance of MOS capacitor in the accumulation region with a 10 V voltage versus testing frequency is shown in Fig.7(b). The capacitance decreases slowly with the increase of frequency, which indicates the existence of dielectric frequency-dispersion in the oxide layer. However, the dielectric frequency-dispersion os not obvious until the frequency increases to 1 MHz, indicating the properties of the perfect interfaces between the oxide layer and the Si substrate as well as between the Al electrode and the oxide layer.[29]

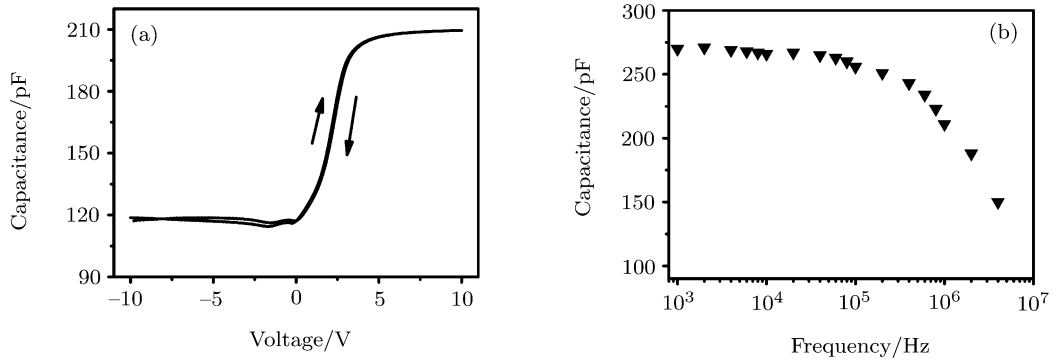


Fig.7. Typical $C-V$ curve of MOS capacitor with oxides oxidized via the O^- anions (a), and capacitance of accumulation region versus testing frequency (b), with the oxidation performed at an O^- anion beam intensity of 0.5 μA/cm^2 and a Si temperature of 300°C.

Figure 8 shows the leakage current density through the MOS capacitor, measured as a function of the applied voltage. The leakage current increases from 10^{-7} A/cm^2 at near 0 V to 10^{-6} A/cm^2 at a bias voltage of 2 MV/cm under a positive bias (the electrons are injected from Si). The leakage current is very low (in the order of 10^{-6} A/cm^2) up to 4 MV/cm, indicating that the oxide layers are possessed of fine insulating properties. The leakage current density gradually increases to 10^{-3} A/cm^2 at 6 MV/cm at a negative bias (the electrons are injected from Al gate). Further work is also required to make clear the mechanism of the electrical feature of the O^--induced oxide layers.

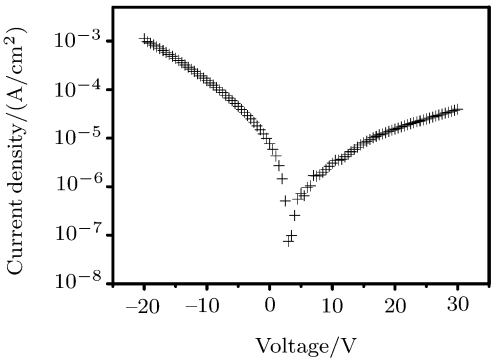


Fig.8. Typical $I-V$ curve of MOS capacitor with oxides oxidized via the O^- anions, with the oxidation performed at an O^- anion beam intensity of $0.5\,\mu A/cm^2$ and a Si temperature of 300°C.

4. Summary

In the present paper, a novel method of performing surface oxidation of Si wafers by O^- anions and fabricating MOS capacitors by the O^--oxidized Si substrates has been investigated for the first time. A highly pure and stable O^- anion beam is generated by using the O^- storage-emission material of C12A7-O^-. The oxidation layer of the Si wafers can be realized in a relatively low temperature region. The surface oxide layer mainly contains SiO_2 together with a small amount of Si_2O_3, and Si_2O. The MOS capacitors of <Al electrode/SiO_x (O^--induced oxide layer)/Si> manifest a good MOS behaviour and have a very low leakage current density that is in the order of $10^{-6}\,A/cm^2$ below $4\,MV/cm$. The O^- anions formed by the present method would have applications to the oxidation and the surface-modifications of semiconductor materials together with the preparation of semiconductor devices.

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