Metal-Insulator-Gap-Insulator-Semiconductor structure for Biological Sensors

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A metal-insulator-gap-insulator-semiconductor sensing device has been characterized in different pH solutions and with different single strand DNA solutions by capacitance-voltage measurements. The capacitance-voltage curves show the difference from pH and the difference from DNA base by hysteresis and flat band voltage shift due to mobile ionic charge in the solution. As the pH decreases, the flat band voltage shift increases in the pH range of 2.7 to 7.0. The hysteresis in the capacitance-voltage curves shows the influence of ionic charge in the solutions and the change of the sensing surface condition. The difference of the flat band voltage shift in the capacitance-voltage curves is related to the mobile ionic charge in the solutions due to pH or DNA molecules.

INTRODUCTION

Recently, a study of detection of deoxyribonucleic acid (DNA) has been advanced as technology to enable genetic diagnosis. Determination of deoxyribonucleic acid (DNA) sequence in biological samples can lead to detection and identification of certain infectious or inherited disease. Especially, the detection of DNA polymorphism that indicates individual differences enables the proper use of drugs or personal diagnostics. Many types of DNA chips and DNA sequencers have been developed. They have been based on fluorescence analyses, mass spectrometry, gel electrophoresis and electrical detection. The electrical detection of DNA has received attention as an alternative to fluorescence analyses, mass spectrometry or gel electrophoresis because of easy miniaturization of electrical detection systems, simple detection process and low cost.

Various types of highly sensitive sequencers using the electrical detection have been developed so far [1]. A field-effect sensor is based on an electrolyte-insulator-semiconductor (EIS) structure. Variations in the insulator-electrolyte surface potential, arise from the binding of molecules, for example nucleic acid, to the insulator surface. The surface potential can be measured by changes in capacitance in the semiconductor part of the EIS device. We have chosen to measure the capacitance because it requires only one electrical connection to the semiconductor. The measured capacitance between the semiconductor and the electrode is dominated by the insulator capacitance and the capacitance of charge in the semiconductor. These capacitances appear in series, and only the semiconductor depletion capacitance is modulated by the insulator surface potential. The capacitance-voltage of the EIS device is similar to that of a metal-oxide-semiconductor (MOS) device [2].
In this study, we have fabricated a metal-insulator-gap-insulator-semiconductor sensing device. This sensing device has the advantage of fewer fabrication processes and low cost. We have demonstrated that the metal-insulator-gap-insulator-semiconductor sensing device can detect and distinguish acetic acid with different pH and label-free 100-base single strand DNA (ssDNA) molecules. We have characterized these solutions in the gap of the sensing device by capacitance-voltage (C-V) measurements.

**EXPERIMENTAL**

Figure 1 shows the schematic of the sensing device with an Al/SiO$_2$/gap/SiO$_2$/n-Si/Al structure. The wafers used in this experiment were the phosphorus-doped n-type Cz Si (100) with a resistivity of 10-20 $\Omega$-cm. The wafer was rinsed with ozonized ultrapure water (5 ppm), cleaned with a 0.25 % HF/0.15 % H$_2$O$_2$/H$_2$O/surfactant solution under megasonic irradiation, rinsed with ozonized ultrapure water (5 ppm), etched with a 0.1 % HF solution, and rinsed with ultrapure water [3]. A thermal SiO$_2$ film as a spacer was formed on n-Si at 1000 $^\circ$C in wet oxygen gas at an atmospheric pressure. The SiO$_2$ film thickness was approximately 600 nm, as measured by ellipsometry. The SiO$_2$ film was patterned by photolithography to define the sensing gap region. The cross sectional area of sensing gap is 600 nm $\times$ 18 mm. A thermal SiO$_2$ film for a sensing surface was formed on the sensing gap surface of n-Si at 1000 $^\circ$C in dry oxygen gas at an atmospheric pressure. The SiO$_2$ film thickness was approximately 20 nm. Aluminum (Al) was evaporated on the back side surface of the n-Si wafer to form a contact electrode. A quartz substrate was chemically cleaned with a 4 vol 97 % H$_2$SO$_4$/1 vol 30 % H$_2$O$_2$
solution and etched with a 0.5 % HF solution. Al was evaporated on the quartz surface to form a contact electrode. The SiO$_2$ film for a sensing surface was formed on the Al electrode using spin on glass (SOG) [4]. The quartz substrate and Si wafer were stacked and fixed with an insulating clamp. In this way, we fabricated the sensing device with the Al/SiO$_2$ (SOG)/gap/thermal SiO$_2$/n-Si/Al structure.

The electrical characteristics were measured by using a Hewlett-Packard model 4284A LCR meter. The sensing device was connected to the multifrequency LCR meter controlled by a personal computer with a GPIB user interface which allows to control experimental parameters and collects the data from the LCR meter. The capacitance-voltage characteristics were measured at 1 MHz. A voltage was applied to the contact electrode on the quartz substrate at the sweep rate of 0.1 V/sec.
RESULTS AND DISCUSSION

Figure 2 shows the cross sectional image of the sensing device with an Al/SiO₂/gap/SiO₂/n-Si/Al structure by scanning electron microscopy. The sensing gap width is confirmed to be approximately 1.4 µm and the SOG layer thickness is approximately 300 nm. Although the thickness of the thermal SiO₂ film as a spacer was approximately 600 nm, the gap width is approximately 1.4 µm because the SOG SiO₂ film has the surface roughness with several hundred nm scale. It can be confirmed that the sensing gap has been fabricated to introduce solutions.

The C-V characteristics at 1 MHz after dipping the sensing gap portion in ultrapure water are shows in Fig. 3. The capacitance at positive voltage (that is the accumulation capacitance) was increased by dipping in ultrapure water because the dielectric constant of ultrapure water is higher than that of the air. The C-V curve has the hysteresis due to mobile ionic charge. This result suggests that the hysteresis is arisen from dissociation and adsorption of silanol groups in the sensing SiO₂ surface [5,6].

The sensing surface was covered by the thermal SiO₂ of 20 nm thickness. The SiO₂ surface has silanol groups. The silanol groups on the SiO₂ surface are dissociation and adsorption sites of protons in solutions. For a return sweep from 10 V to -10 V, protons in

Fig.3 Capacitance-voltage curves at 1 MHz after dipping sensing gap portion in ultrapure water.
solutions were moved close to the sensing surface and protons were adsorbed to silanol groups. While on a forward sweep from -10 V to 10 V, hydroxide ions in solutions were moved close to the sensing surface and protons were dissociated from silanol groups. The sensing surface was charged by negative charge and the flatband voltage was shifted toward the positive voltage. Then, the C-V curve has the hysteresis due to mobile ionic charge.

The C-V characteristics at 1 MHz after dipping the sensing gap portion in 1.17×10^{-5}, 2.28×10^{-3}, and 2.85×10^{-1} mol/L acetic acid solutions with ultrapure water solvent and ultrapure water are shown in Fig.4. These acetic acid solutions have a pH of 4.9, 3.7, and 2.7, respectively. The accumulation capacitance increases with increasing the concentration of acetic acid because the dielectric constant of the acetic acid solution increases. The hysteresis due to mobile ionic charge is observed in the C-V curves. It is considered that the hysteresis arises from dissociation and adsorption of silanol groups on the SiO$_2$ surface. The C-V curves for forward sweeps after dipping in the acetic acid solutions are shifted toward the negative voltage, compared with the C-V curve after dipping in the ultrapure water. The C-V curves shift toward the negative voltage as the concentration of acetic acid increases. This result suggests that the voltage shift toward the negative voltage reflects the negative charge decrease of silanol groups in the sensing SiO$_2$ surface by the increase of protons in acetic acid solutions.
Fig. 5. Capacitance-voltage curves at 1 MHz after dripping sensing gap portion in DNA solutions.

The C-V characteristics at 1 MHz after dipping the sensing gap portion in T100, A100, and G100 ssDNA solutions with ultrapure water solvent and ultrapure water are shown in Fig. 5. The C-V curves have the hysteresis due to mobile ionic charge. The C-V curves for forward sweeps after dipping sensing gap portion in the DNA solutions are shifted toward the negative voltage compared with ultrapure water. This result suggests that the flatband voltage shift toward the negative voltage reflects the negative charge decrease of silanol groups in the SiO2 surface by the negative charge of ssDNA molecules in the solutions. It is confirmed that the DNA solution can be detected by C-V measurements.

CONCLUSION

We have demonstrated that the sensing of acetic acid solutions and DNA solutions by the flatband voltage shift in C-V characteristics of the sensing device with the Al/SiO2/gap/SiO2/n-type Si/Al structure. The hysteresis due to mobile ionic charge is observed in the C-V characteristics. The ssDNA solutions can be detected from the flatband voltage shift. It is suggested that the hysteresis arises from dissociation and adsorption of silanol groups in the sensing SiO2 surface and the flatband voltage shift toward the negative voltage reflects the negative charge decrease of silanol groups in the sensing surface by the negative charge of DNA molecules in the solution. The metal-
insulator-gap-insulator-semiconductor sensing device has the possibility for the detection of DNA molecules.

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