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Crown-Ether Cyanide Treatment to Eliminate Interface States at Si/SiO_2 Interfaces

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1.Introduction

Interface states in the Si band-gap play an important role in the determination of electrical characteristics of MOS devices. Interface states are usually eliminated by heat treatment at 300~500 ºC in hydrogen, which results in Si-H bonds from Si dangling bonds [1,2]. This method has disadvantage that heat treatment cannot be performed after the hydrogen treatment because the Si-H bonds are ruptured above 550~600 ºC [3,4]. Irradiation also induces interface states because hydrogen atoms generated in the SiO_2 layers by the irradiation react with Si-H species at the interfaces, resulting in the formation of the Si dangling bonds [5,6]. Therefore, a method to eliminate the interface states with no use of hydrogen is favored.

In the present study, we have developed a method to eliminate the interface states by the formation of Si-CN bonds at the interface using cyanide method, i.e., the immersion of Si in a KCN solution followed by the rinse in water. The contamination by K^+ ions is avoided by the addition of crown-ether in the KCN solution, which effectively captures K^+ ions.

2.Experiments

After cleaning phosphorus-doped n-type Si(100) wafers with a resistivity of ~1 Ωcm, the wafers were immersed in a KCN solution prepared as follows. 0.2 mole of 18-crown-6 ($C_{12}H_{24}O_6$) was dissolved in xylene and the solution was mixed with a 0.1 M KCN aqueous solution. After stirring intensively, the part of the xylene solution which was well separated from the aqueous solution was used for the cyanide treatment. The Si wafers were immersed in the KCN solution thus prepared for 2 min and rinsed in ultra-pure water at 25 ºC for 10 min. Then, the Si wafers were heated at 450 ºC in oxygen and then indium tin oxide (ITO) layer was deposited by a spray pyrolysis method [7] to form MOS structure.

Capacitance-voltage (C-V) and conductance-voltage (G-V) measurements were performed at the frequency of 1 kHz.

3.Results and discussion

Figure 1 shows the G-V curves for the <ITO/SiO_2/Si(100)> MOS structure. The thickness of the SiO_2 layer was estimated to be 2.5 nm from the XPS spectra in the Si 2p region. Due to the ultrathin oxide layer, a high density tunneling current flows in the negative (forward) bias region, leading to an increase in the conductance. In the positive bias region, on the other hand, the main conductance is due to interface states.

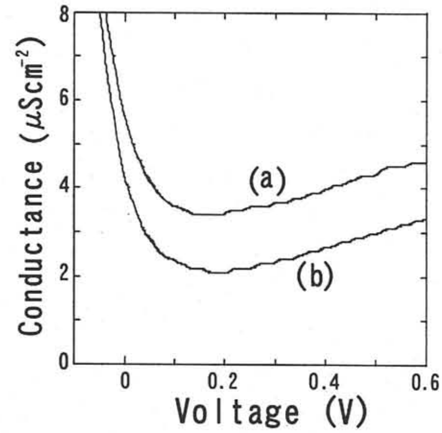

Fig. 1 G-V curves for the <ITO/SiO_2/Si(100)> MOS structure: a) without the cyanide treatment; b) with the crown-ether cyanide treatment.

Without the cyanide treatment (curve a), the conductance due to the interface states was high. The conductance due to the interface states decreased markedly by the cyanide treatment (curve b).

Figure 2 shows the C-V curves measured at 130 ºC. Without the cyanide treatment, hysteresis with the magnitude of ~0.1V was present in the curve (curve a). The hysteresis is likely to be caused by slow interface states [8]. When the specimens were treated with a KCN solution containing no crown-ether, i.e., immersion in the 0.1 M aqueous solution followed by the rinse in boiling water for 10 min [9], the hysteresis was also observed (curve b). It should be noted that the cyanide treatment without crown-ether decreased the interface state conductance and the hysteresis was not observed at 25 ºC. Therefore, the hysteresis is attributable to mobile ions, i.e., K^+ ions, in the oxide layer. From the magnitude of the hysteresis of ~0.1 V, the amount of K^+ ions is estimated to be $2x10^{10}cm^{-2}$ assuming that K^+ ions move between the SiO_2/Si and ITO/Si interfaces by the change in the bias voltage.

When the cyanide treatment was performed using the KCN

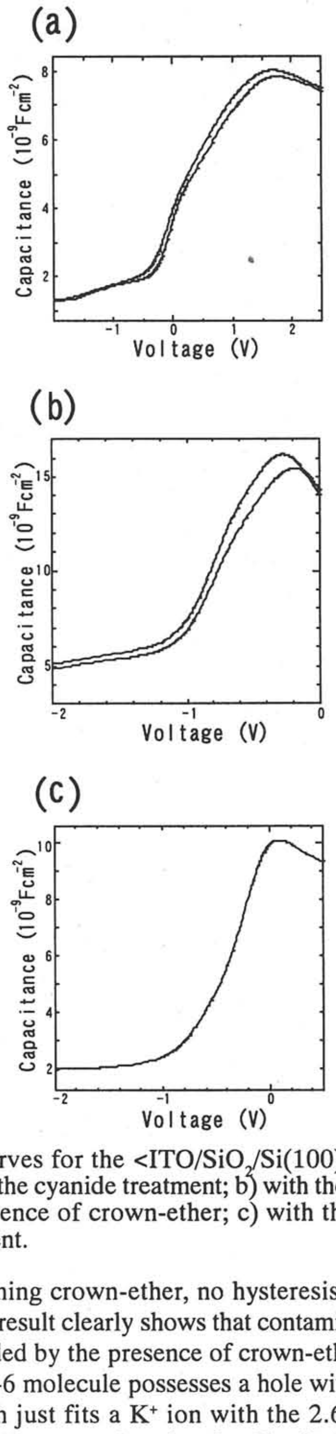

Fig. 2 C-V curves for the <ITO/SiO_2/Si(100)> MOS structure: a) without the cyanide treatment; b) with the cyanide treatment in the absence of crown-ether; c) with the crown-ether cyanide treatment.

solution containing crown-ether, no hysteresis was observed (curve c). This result clearly shows that contamination of Si by K^+ ions is avoided by the presence of crown-ether.

A 18-crown-6 molecule possesses a hole with the diameter of 2.7 Å, which just fits a K^+ ion with the 2.66 Å diameter. Therefore, the 18-crown-6 molecule effectively captures the K^+ ion, avoiding the direct contact of K^+ ions with Si. On the other hand, CN^- ions are well separated from K^+ ions, and consequently the reactivity of CN^- ions increases. CN^- ions are likely to form strong bonds with defects such as Si dangling bonds because they have metallic character to some extent, and consequently defect states are removed from the Si band-gap [8].

Figure 3 shows the photocurrent-photovoltage (I_{ph}-V_{ph}) curves for the <ITO/SiO_2/Si(100)> MOS structure. The thickness of the SiO_2 layer was reduced to ~1.5 nm, and thus a pho-

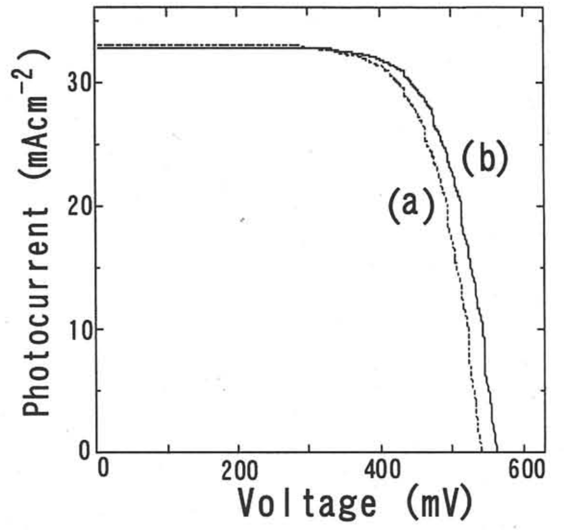

Fig. 3 Photocurrent-photovoltage curves for the <ITO/SiO_2/Si(100)> MOS tunneling diodes: a) without the cyanide treatment; b) with the crown-ether cyanide treatment.

tocurrent flew easily though the SiO_2 layer. With the cyanide treatment, the photovoltage increased by 40 mV. From this increase, the dark current density is estimated to decrease to ~1/5, which is caused by the reduction in the interface state density. Namely, the decrease in the interface state density increases the band-bending in Si and decreases the interface state recombination current density, and consequently the electrical characteristics of the MOS tunneling diodes are improved.

4.Conclusion

The crown-ether cyanide treatment, i.e., the immersion of Si in the KCN solution containing 18-crown-6, is found to eliminate the interface states present at the Si/SiO_2 interface, and the electrical characteristics of the MOS tunneling diodes are improved. Crown-ether effectively captures K^+ ions, and consequently contamination of Si by K^+ ions is avoided.

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