$(NH_4)_2S$ treatment of the Si (100) surface and its effects on Al/Si Schottky barrier heights*

Hu Aibin(胡爱斌)†, Wang Wenwu(王文武), and Xu Qiuxia(徐秋霞)

(Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China)

Abstract: The effect of Si (100) surface S passivation was investigated. A thick film with a high roughness value was formed on the Si surface treated by $(NH_4)_2S$ solution, which was attributed to physical adsorption of S atoms. SEM and XPS analyses reveal that Si surface atoms were chemically bonded with S atoms after Si surface treatment in NH_4OH and $(NH_4)_2S$ mixing solution. This induces a more ideal value for the Schottky barrier height compared with a diode treated only by HF solution, indicating that surface states originating from dangling bonds are passivated with S atoms.

Key words: Schottky barrier; $(NH_4)_2S$ treatment; dangling bonds; *I–V*
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1. Introduction

Schottky barrier height is an important parameter in metal–semiconductor systems. Ideally, barrier height is determined by the metal work function and the electron affinity of the semiconductor. In reality, the surface states between the metal and the semiconductor pin the Fermi level at the interface, which make the barrier height less sensitive to the metal work function[1]. Figure 1(a) shows the atomic structure of a cleaned Si (100) surface in vacuum. The surface has to undergo reconstruction due to the discontinuity of the lattice atoms on the surface. Each surface atom has a dangling bond and shares a dimer bond with its neighbor atom, which gives rise to surface states within the Si bandgap[2].

Kaxiras theoretically introduced a concept of "valence-mending" to passivate the Si (100) surface[3]. As shown in Fig. 1(b), for the Si (100) surface, a S or Se atom can take the bridge position between two surface atoms; therefore it can nicely terminate dangling bonds and relax strained dimer bonds. Papageorgopoulos experimentally studied Si (100) 2×1 surface restoration by adsorption of elemental S[4]. Passivation of III–V semiconductor surfaces using $(NH_4)_2S$ solution has been widely studied[5]. Ali has studied Si (100) S passivation using $(NH_4)_2S$ solution, but physical analysis of S passivation was not shown in Ref. [6].

In this paper, the Si (100) surface treated in $(NH_4)_2S$ solution was analyzed using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). A simple wet chemical method was given to passivate the Si (100) surface and its effect on the Schottky barrier was investigated.

2. Experiment

N-type or P-type Si (100) wafers with resistivities of about 1–4 Ω·cm were used for the experiments. After standard RCA cleaning, the wafers were treated in a solution containing $(NH_4)_2S$ (S-treated sample), where the volume fraction of $(NH_4)_2S$ is about 1%. The control wafers were dipped in 1% HF acid for 60 s to strip native oxide (HF-treated sample). About 2000 Å Al was deposited and patterned. The Al contact sizes are 100, 200 and 500 μm in diameter. Al was also deposited on the backside of all wafers for backside ohmic contact. Compared to the front contact, the back contact has a larger area, which makes it possible to characterize the front diode with negligible effect from the back contact. The Schottky diodes were characterized by current–voltage (*I–V*) measurements using HP 4200.

3. Results and discussion

After standard RCA cleaning, the Si wafers were wet etched in HF solution to remove native oxide until the surface was hydrophobic and immediately rinsed in DI water and treated in $(NH_4)_2S$ solution at 60 °C for 20 min. It was found that most of the Schottky diodes treated by $(NH_4)_2S$ have nearly the same *I–V* characteristics as the control samples. Figure 2(a) shows the SEM surface morphology of the S-treated Si wafer. Rough film was observed locally on the S-treated Si surface, which was presumably attributed to physically adsorbed amorphous S. Regarding the formation of rough S film, there may be three reasons. Firstly, even if the

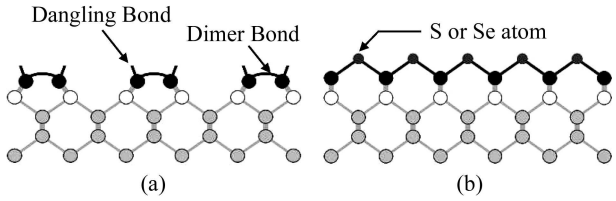

Fig. 1. Atomic structure of (a) a cleaned Si (100) surface in vacuum and (b) a S or Se passivated Si (100) surface.

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† Corresponding author. Email: huaibin@ime.ac.cn
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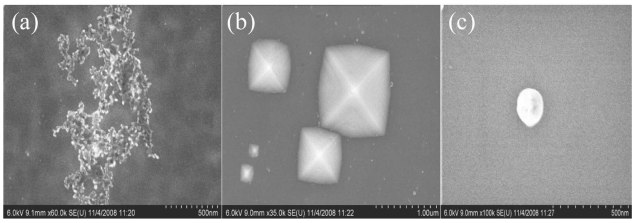

Fig. 2. SEM images of Si (100) surface after $(NH_4)_2S$ treatment. The conditions are: (a) without NH_4OH added at 60 °C for 20 min; (b) with NH_4OH added at 60 °C for 20 min; (c) with NH_4OH added at 60 °C for 5 min.

native oxide layer on the Si wafer is removed by acid solutions such as HF, the clean Si surface may still be reoxidized when the wafer is dipped in DI water or during transport to the next solution. Consequently, the reformed oxide layer on the Si surface restricts chemical bonding between the Si and S atoms, and physical adsorption of the S atoms dominates the Si surface. Secondly, the dangling bonds, in theory, are almost passivated with hydrogen atoms after dilute HF cleaning, but actually there may be some other atom groups on the HF etched Si surface[7], which constrains S atoms bonding with the Si surface, and the S atoms are only physically adsorbed on the Si surface. Lastly, $(NH_4)_2S$ solution is thermally unstable at temperatures higher than 40 °C, so in our condition the decomposed S atoms can be deposited or physically adsorbed on the Si surface.

In order to solve this problem, an etchant for SiO_2 and Si, NH_4OH[8, 9], was added into the solution, which can also restrict the hydrolyzation of $(NH_4)_2S$. The volume fraction of NH_4OH is about 5%. First, the Si wafer was dipped in HF acid to strip the native oxide, then a thin fresh oxide layer was grown using rapid thermal anneal at 900 °C for 60 s. The wafers were then treated in $(NH_4)_2S$ solution mixed with NH_4OH. By growing the thin oxide layer and then *in situ* etching it in the solution, our process has the inherent advantage of removing carbon along with other contaminants. Figure 2(b) shows the SEM image of the Si wafer treated in $(NH_4)_2S$ solution with NH_4OH added at 60 °C for 20 min. The result is completely different from that shown in Fig. 2(a). There are many crystal grains with different sizes on the Si surface. EDX analysis shows that the grains are mainly composed of the S atoms. It is believed that the S atoms were first "grown" in two dimensions and then three-dimensional islands formed through the Volmer–Weber growth mode which was driven by surface energy[10]. The reaction time in Fig. 2(b) was too long, so we need to reduce the S-treatment time to avoid the growth of the S crystal grains. Figure 2(c) shows the SEM image of Si wafer treated in $(NH_4)_2S$ solution with NH_4OH added at 60 °C for 5 min. There is a contaminated particle in the center. Neither amorphous S nor S crystal grains were observed in this condition.

Typical surface Si2p and S2p XPS spectra are shown in Fig. 3, where the Si wafer was treated with $(NH_4)_2S$ solution under the same conditions in Fig. 2(c). The binding energy was calibrated with C1s = 284.5 eV. A strong S2p signal was detected, as shown in the inset of Fig. 3. It is clearly observed in

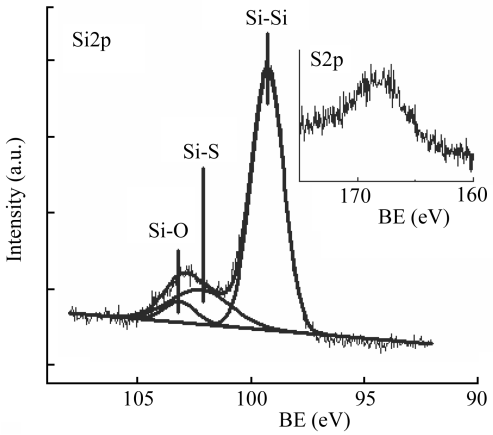

Fig. 3. XPS spectrum of Si2p. The inset shows the S2p spectrum. The Si wafer was treated in $(NH_4)_2S$ solution with NH_4OH added at 60 °C for 5 min.

Fig. 3 that the Si2p spectrum is composed of mainly bulk components (Si–Si bond) with a binding energy of 99.3 eV[11] and other chemically shifted components. Because of the existence of a strong S2p signal and a relatively small O1s signal, we put the Si–S bond and Si–O bond components in peak decomposition. As shown in Fig. 3, the Si2p spectrum was decomposed into three peaks: Si–Si bond, Si–S bond and Si–O bond peaks with binding energies of 99.3, 102.2 and 103.1 eV[11, 12], respectively. Our sample was exposed to air for several days before XPS measurement, which may cause surface Si–S bond oxidization. The peak area of the Si–S bond is much larger than that of the Si–O bond, as shown in Fig. 3. It is believed that the predominant Si chemical state on the surface is S coordinated Si which has a potential to eliminate surface dangling bonds and strained dimer bonds on the Si (100) surface. Using this S-treatment condition, we have fabricated Al/n-Si and Al/p-Si Schottky diodes.

Figures 4(a) and 4(b) show the *I*–*V* characteristics of HF-treated and S-treated Al/n-Si Schottky diodes, respectively. In Fig. 4(b), the current is almost proportional to the voltage in the forward and reverse bias, respectively. As our substrate doping is only about 10^{16} cm^{-3}, it is believed that thermionic emission is the dominant current transport mechanism, except that the Schottky barrier height is lower than that we commonly get, as shown in Fig. 4(a). As shown in Fig. 4(b), once the applied voltage exceeds the barrier height, the diode becomes ohmic.

Figures 5(a) and 5(b) show the *I*–*V* characteristics of HF-treated and S-treated Al/p-Si Schottky diodes, respectively. The HF-treated diode behaves as an ohmic contact while the S-treated diode behaves as a Schottky contact. Compare to the HF-treated diode, the Schottky barrier height of the S-treated diode is increased. We use the common thermionic emission model[1] to fit the forward *I*–*V* curve (forward voltage from 0.2 to 0.5 V) of Fig. 4(a) and Fig. 5(b). The equation is as follows:

$$I = A^* T^2 \exp\left(-\frac{\phi_B}{V_T}\right)\left[\exp\left(\frac{V - IR}{nV_T}\right) - 1\right]. \quad (1)$$

Here A^* is the effective Richardson constant; T is the

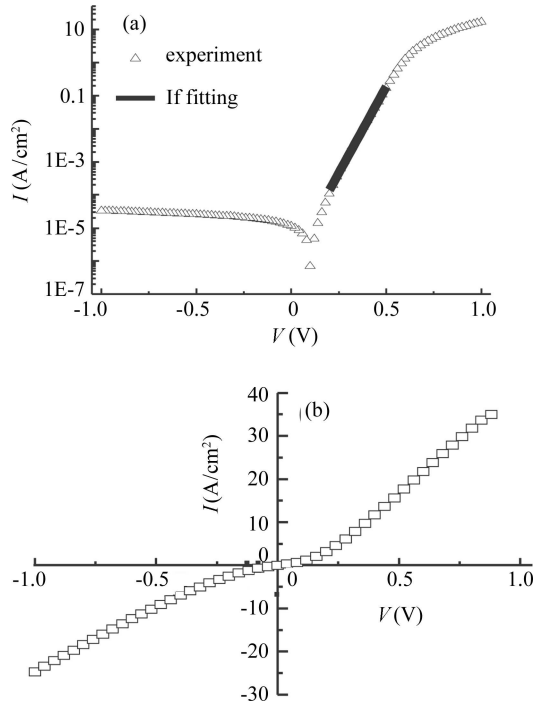

Fig. 4. *I–V* characteristics of (a) HF-treated and (b) S-treated Al/n-Si Schottky diodes.

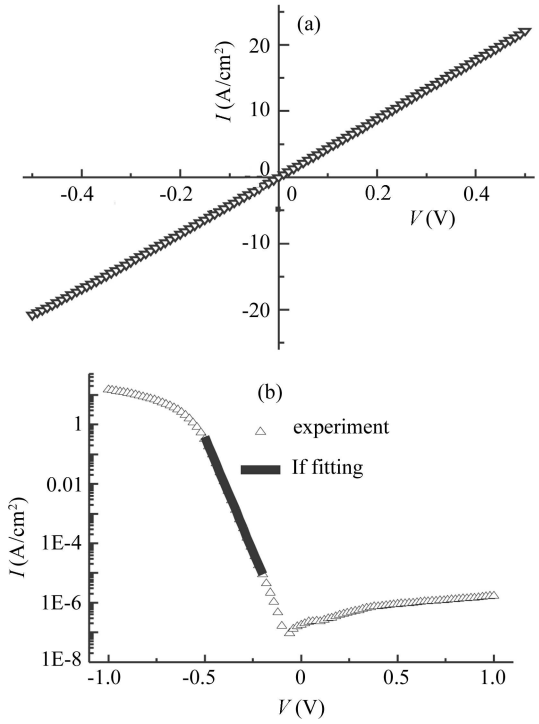

Fig. 5. *I–V* characteristics of (a) HF-treated and (b) S-treated Al/p-Si Schottky diodes.

temperature in Kelvin; $V_T = kT/q$ is the thermal voltage; n is the ideality factor and R is the series resistance; Φ_B is Φ_{Bn} or Φ_{Bp}, where Φ_{Bn} (Φ_{Bp}) is the Schottky barrier height between Al and n-Si (p-Si). Φ_B, n and R are unknown parameters and will be fitted using Eq. (1). All the constants are taken from Ref. [1]. Schottky barrier lowering due to the image force effect is not considered in Eq. (1). The fitting results of forward current (I_f) are also shown in Fig. 4(a) and Fig. 5(b). If we get

Table 1. Schottky barrier height fitting results and calculated ideal values.

SBH (V)	HF-treated diode	S-treated diode	Ideal value
Φ_{Bn}	0.80	0.22	0.15
Φ_{Bp}	0.32	0.90	0.97

either Φ_{Bn} or Φ_{Bp}, then anther one can be calculated using:

$$\Phi_{Bn} + \Phi_{Bp} = E_g/q, \tag{2}$$

where E_g is the bandgap of Si[1].

Table 1 shows the fitted Schottky barrier height (SBH) and the ideal values. The work function of Al is taken as 4.2 eV[13], and the electron affinity of Si is taken as 4.05 eV[1]. The Φ_{Bn} (Φ_{Bp}) of the HF-treated Schottky diode is 0.80 V (0.32 V), which is much larger (smaller) than the ideal value of 0.15 V (0.97 V), indicating that SBH is determined mainly by the surface states. Electrically, surface states originated from dangling bonds often pin the surface Fermi level, causing the Schottky barrier height to be less sensitive to the metal work function[14]. Compared to the HF-treated Schottky diode, the Φ_{Bn} (Φ_{Bp}) of the S-treated Schottky diode is 0.22 V (0.90 V), which is closer to the ideal value of 0.15 V (0.97 V). Based on theoretical calculations[3, 15], when the dangling bonds were passivated by S atoms, surface states can be reduced. Clearly, a nearly ideal Al/Si Schottky barrier height was obtained by S passivation in our experiments.

4. Summary

In this letter, a novel Si (100) surface "*in situ* etch and passivation" method, in which NH_4OH was added to $(NH_4)_2S$ solution, was given. SEM and XPS analyses show that Si dangling bonds were passivated by S atoms. HF-treated and S-treated Al/n-Si and Al/p-Si Schottky diodes have been fabricated and Schottky barrier heights were fitted using the *I–V* method. Our experimental results indicate that surface states originating from dangling bonds were passivated with the S atoms.

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