第20卷第4期 半导体学报 Vol. 20, No. 4
1999年4月 CHINESE JOURNAL OF SEMICONDUCTORS Apr., 1999

Study on Interfacial SiO_2 Layer of Silicon Direct Bonding*

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Abstract The interfacial SiO_2 layer of silicon direct bonding has been studied in this paper. By means of AES (Auger Electron Spectrum) and SEM (Scanning Electron Microscope), it has been found experimentally that interfacial SiO_2 disintegrates into sphere-shaped-like islands with average radius much larger than L, the thickness of the native oxide layer, and is of amorphous material, $SiO_{1.5}$. The theoretical analysis shows that SiO_2 spontaneously disintegrates into islands because the interface free energy will decrease as much as possible.

PACC: 6845, 8265, 3520G

1 Introduction

In recent years silicon direct bonding (SDB) has been demonstrated as a promising technology for MEMS (micro-electron-machine-system), SOI (silicon-on-insulator), DI (dielectric-insulator) and PE (power electronics), etc.[1,2]. The bonding interface (BI) plays an important role in determining the electrical properties of SDB devices. Depending on the specific application, a continuous and uniform SiO_2 layer is required (SOI and DI) or just opposite of it (PE and MEMS). Some papers in the literatures demonstrated the existence of a 0.5~4.5nm thick, continuous and uniform, interfacial SiO_2 layer at BI after heat-treatment for SDB[3~5]. On the other hand, other papers reported no SiO_2 layer at BI[6,7]. Nonetheless, the structure and existence of the interfacial SiO_2 layer are very complex and involve uncertainties. In order to get a better understanding of the characteristics of the BI, the structure and instability of the SiO_2 layer have been studied experimentally and theoretically in this paper.

2 Experimental

The n-type FZ Si (100) wafers, 76.2mm in diameter, with the resistivity of 1~5

* This work was supported by the National Natural Science Foundation of China (Grant No. 69776041).
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Received 2 September 1998, revised manuscript received 21 December 1998

Ω · cm and with a thickness of 380±20μm, were used as the starting material. The wafers were polished and cleaned to have flat surfaces, free of contamination. After cleaning by dipping in a diluted HF : H_2O solution followed by the standard RCA cleaning procedure, they were immersed in H_2SO_4 : H_2O_2 solution of 70℃ for 20min to form a hydrophilic surface. Then, after rinsing in de-ionized water, they are brought together at room temperature to perform the prebonding. The wafers, held together by adhesive forces, were then moved to a flat boat and loaded into an annealing furnace. To turn weak prebonding into a strong chemical bond, the wafer pairs were annealed for 2～4 hours at the process temperature, 1180℃, in an oxidizing ambient. Following the above procedure, the successful SDB were performed. Finally, bonding pairs were cut into pieces of 1×1cm² for testing and analysis.

3 Results

The BI of bonding pairs are enlarged by cross-section beveling technique. AES (Auger Electron Spectrum) cross-section observations are obtained by AES-450, as shown in Figs. 1 and 2. We use the symbols of a-a' and b-b' to represent the different positions of the identical BI of the bonding pairs.

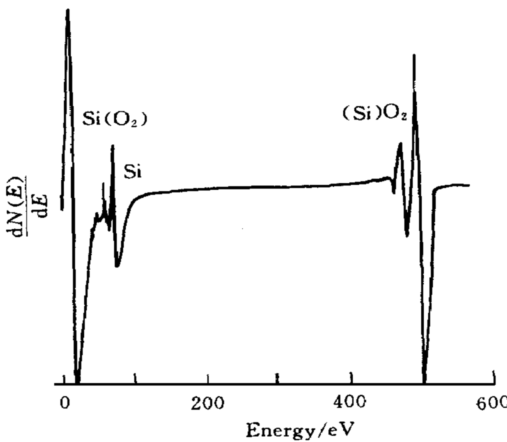

Fig. 1 Pan-spectrum of AES of the BI

From Fig. 1, it is found that Si(O) peak exists at 72eV, silicon peak is present at 83eV and 93eV, while oxygen peak shows at 500eV. It can be concluded that the BI consists of Si(O), Si and O_i.

From Fig. 2, it is found that, at the identical BI, atom concentration percentage (ACP) of Si(O), Si and O_i varies locally with the distance, and the ratio of Si(O) to O_i is about 1 : 1.5. We can conclude that the Si(O) profile is non-uniform but continuous every where at the identical BI, and the structure of the interfacial SiO_2 is amorphous, $SiO_{1.5}$.

In order to get the detailed information of the distribution of the interfacial SiO_2, the high-resolution (3nm) SEM (Scanning Electron Microscope) observation is performed by XL-300. The condition and results are shown in Fig. 3 (a) and (b).

From Fig. 3, it is found that the interfacial SiO_2 layer disintegrates into sphere-shaped-like islands with average radius of 20～30nm. The growth of interfacial SiO_2 seems to occur in certain places. Whereas, the epitaxy-like silicon occurs in other places. The above results indicate that no SiO_2 exisfs in uniformity and continuum. This is in accord with those obtained by AES.

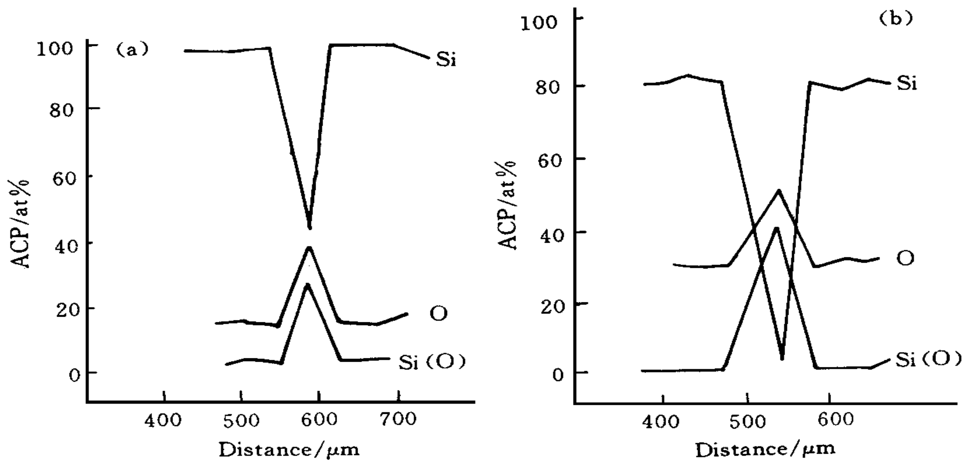

Fig. 2 (a) Scanning AES for *a*-*a*'; (b) Scanning AES for *b*-*b*'

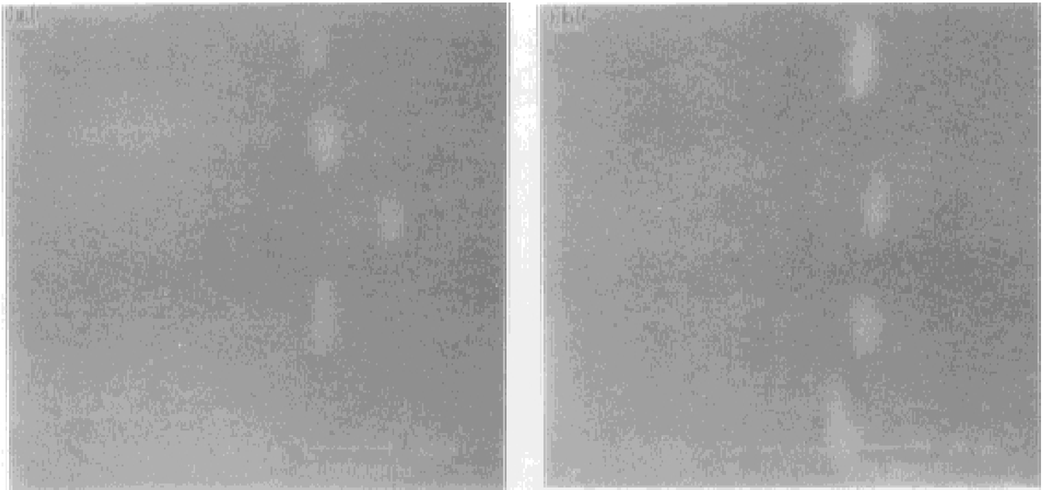

Fig. 3 (a) SEM for samples treated at 1180℃ for 2h,
(b) SEM for samples treated at 1180℃ for 4h

4 Discussion

First, consider the possibility of the dissolution of the interfacial SiO_2 layer by the diffusion of oxygen interstitial, O_i, into the silicon wafer. Based on Ref. [8], the dissolvable thickness $X(t, T)$ may be written as

$$X(t, T) = [D(T)t/\pi]^{1/2}[4C_i^{eq}(T)/n_{ox}] \quad (1)$$

for the typical annealing temperature, 1180℃ and time, 2~4h. The interfacial SiO_2 should be completely dissolved. However, it is not compatible with the above AES and SEM, and cannot explain the spheroidization of the interfacial SiO_2.

More likely the process of the interfacial SiO_2 layer spheroidizatoin is the growth of SiO_2 by the reduction of interface energy. Since the initial disintegration of SiO_2 may begin

with forming silicon holes in the SiO_2 layer[9], the epitaxy-like silicon micro-region will form with the disintegration of SiO_2. This process, very well, coincides with the SEM. Interface energy change can be given by the following equation based on the classical nucleation theory [10]

$$dG = \sigma dA = f(T) 4\pi r^2 dr \quad (2)$$

The above equation indicates that the reduction in the surface area of the interfacial SiO_2 leyer can effectively lower the interface energy, and critical radius r_c is reached when the interfacial SiO_2 is in equilibrium with its environment, or $dG = 0$.

To calculate r_c, in a simply way, the equilibrium surface area of SiO_2 is assumed to be $\eta(T)$ times less than the initial, $\eta(T)$ is called the equilibrium interface factor. It is evident that the higher the annealing temperature, the larger the $\eta(T)$.

The interfacial SiO_2 can lower its interface energy to a maximum extent and the equilibrium with its environment is satisfied by spheroidization when

$$1 - 2\pi r_c^2 N \eta(T) = 0 \quad (3)$$

where N is the number of SiO_2 islands with critical radius r_c per unit surface area.

In the first-order approximation, the volume variation of SiO_2 with thickness L should keep a constant

$$N (4/3) \pi r_c^3 = L \quad (4)$$

where L being the thickness of the native oxide layer of silicon, about 4nm. Combing Eqs (3) and (4) gives

$$r_c = 1.5 \eta(T) L \quad (5)$$

At the extreme situation, the minimal radius r_c^{min} of SiO_2 islands can be given by the following form

$$r_c^{min} = 1.5L \quad (6)$$

which is just the same result given in Ref. [8].

Since the driving force of spheroidiztion is the reduction of interface energy, or surface area of the interfacial SiO_2, $\eta(T)$ must be larger than 1. Taking into account the dissolution of SiO_2 by oxygen diffusion, the equation including the above two effects can be written as

$$r = 1.5 \eta(T) L - [D(T) t/\pi]^{1/2} [4C_i^{eq}(T)/n_{ox}] \quad (7)$$

At the annealing tempeerature, 1180°C, if $\eta(T)$ is assumed to be 12, theoretical calculation of r_c given by Eq. (7) is 26nm for 4h and 21nm for 2h respectively, which are in agreement with the results of SEM.

5 Conclusion

The interfacial SiO_2 layer of SDB has been investigated experimentally and theoretically, main results are as follows

(1) The structure of the interfacial SiO_2 is amorphous, $SiO_{1.5}$;

(2) Existence of the interfacial SiO_2 in the form of sphere-shaped-like islands results

from the effect of reduction in the surface area of SiO_2;

(3) The theoretical calculation of critical radius r_c of SiO_2 is in good agreement with the results of SEM by setting the equilibrium interface factor being 12 at the annealing temperature, 1180℃.

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