XPS STUDIES OF IRRADIATED HARD AND SOFT $Si-SiO_2$*

Liu Changshi (刘昶时)
(*Xinjiang Institute of Physics, Academia Sinica, Urumqi 830011, China*)
Zhao Yuanfu (赵元富)
(*Lishan Institute of Microelectronics, Aero-Space Industry Ministry, Xian 710600, China*)
Wang Zhongyan (王忠燕), Chen Ying (陈 萦), Liu Fen (刘 芬)
and Zhao Ruquan (赵汝权)
(*Beijing Centre of Physical and Chemical Analysis, Beijing 100081, China*)
(Received December 1992)

ABSTRACT

The interfacial structure of hard and soft oxides grown by dry oxidation on <100> n-type silicon substrates is examined using high resolution mild X-ray photoelectron spectroscopy (XPS) before and after irradiation. Substantial differences in silicon of silica state (B.E. 103.4 eV), silicon of transitional state (B.E. 101.5 eV), surplus oxygen (B.E. 529.6 eV) and negative two-valence oxygen (B.E. 531.4 eV) are observed between the two kinds of samples. The XPS spectra strongly depend on the conditions of irradiation for soft samples, but do not as remarkablely as soft samples for hard samples. The effects of irradiation doses on XPS are greater than that of irradiation bias fields. Some viewpoints of irradiation induced hole electron pair are proposed to explain the results.

Keywords: XPS Radiation hard Radiation soft $Si-SiO_2$ Bias field Radiation dose

1 INTRODUCTION

Silicon has been the major integrated-circuit-making material[1] with the basic structure being $Si-SiO_2$. In outer space due to large fluxes of impinging particles (electrons, ions and photons)[2], hence electronic devices degrade the life limit of a space craft. That is why radiation effects on a $Si-SiO_2$ system have been an important subject of irradiation and semiconductor physics[3-5]. In this work, high resolution mild X-ray photoelectron spectroscopy (XPS) is used to examine the interfaces of radiation hard and soft $Si-SiO_2$, which have such structure that the former prepared by specific oxidation process can stand up to a great extent irradiation without

* This work was supported by Beijing Zhongguancun Associated Center of Analysis and Measurement

change in electronic features, while the latter is without such character. Subjects of the stúdy include the environment of fixed atoms, the chemical configurations and irradiation doses, and the bias. The results suggest some useful ways to make radiation hard Si-SiO_2 devices.

2 EXPERIMENT

A SiO_2 film of radiation hard sample with 68 nm in thickness was grown in dry O_2 at 1000 °C on 4.5 Ω · cm n-type silicon (100) substrate, and annealed in N_2 at 900 °C for 30 min. The other SiO_2 film of soft sample with 67 nm in thickness was grown in dry O_2 and 3 % HCl gases at 1000 °C on the same substrate. Al layers were deposited by electron beam on both samples to form MOS capacitors.

The samples were irradiated by ^{60}Co gamma rays at room temperature. The dose ranges from 0 to 100 kGy (Si) with dose rates varying from 0 to 333.3 Gy (Si)/min. The bias fields were 0 and +1 MV/cm respectively. In order to get the targets appropriated for XPS analysis, sulphuric acid and hydrogen peroxide solution was employed to remove the connective layers of Al gate prior to the samples' XPS measuremnt. XPS measurements were conducted on a KRATOS XSAM800 electron spectrometer with a high resolution. Vacuum of the system was better than 2.6 μPa. The samples were excited by 1486.6 eV Al K_α X-ray, and etched with 4 keV Ar^+ beam. The code DS300X Data System was employed for data handling.

3 RESULTS AND DISCUSSION

According to the profile results of radiation hard and soft Si-SiO_2 by XPS, XPS spectra[6] that are basically of the same distance from silicon substrate of every sample were obtained, from which the effect of radiation dose and bias field are considered.

3.1 Effects of dose observed from Fig.1,2

a. The Si 2p XPS spectra of the silica state indicate that SiO_2 composition of soft samples decreases with increasing of doses, at the same time binding energy of Si 2p moves to high energy, while the changes of hard oxides are not as great as that of the soft.

b. Packwood *et al* have pointed out that the peak corresponding to B.E. 101.5 eV Si 2p belongs to SiO_x ($x \approx 1.1$) structure[7]. The soft SiO_x composition decreases slightly with increasing irradiation doses, while with the hard samples it decreases very much. B.E. of the former moves to the low energy, but B.E. of the latter to the high energy.

c. The concentration of surplus oxygen structure (B.E. 529.6 eV)[8,9] in hard Si-SiO_2 systems is lower than that in soft samples before irradiation. When irradiation dose reaches 10 kGy (Si) we cannot observe surplus oxygen in the hard; however the irradiation dose does not influence the content of surplus oxygen in the soft. There is only one kind of oxygen (B.E. 531.4 eV) in the hard Si-SiO_2 irradiated, we can not observe any change of oxygen composition in the soft irradiated. From these, it is concluded that the binding energy of the soft and hard has the tendency to increase.

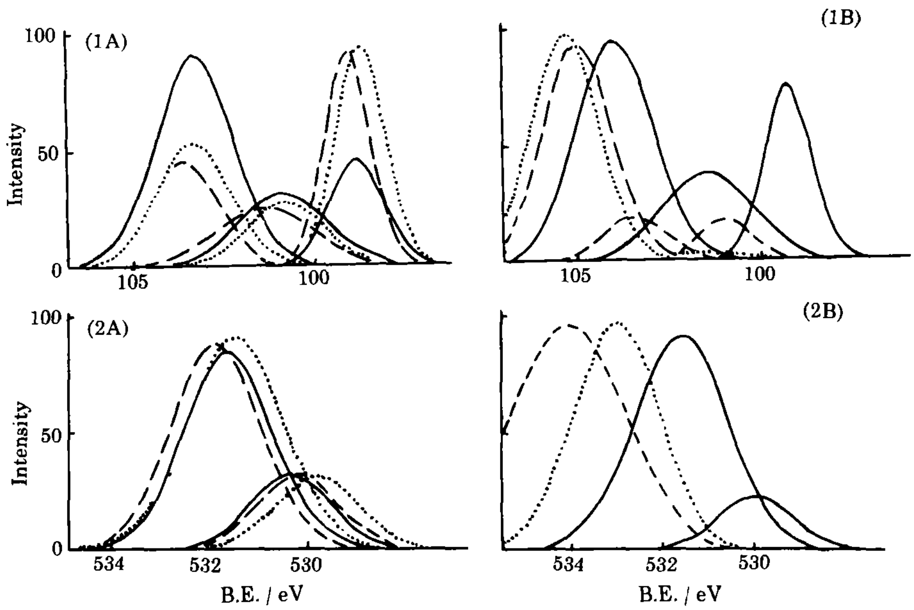

Fig.1,2 Si 2p(1) and O 1s (2) XPS spectra of the samples irradiated under the same bias field

A: Soft oxides B: Hard oxides

— 0 Gy (Si) --- 10 kGy (Si), +1 MV/cm ··· 100 kGy (Si), +1 MV/cm

The interaction between gamma ray and Si-SiO_2 is ionization. It produces electron-hole pairs. The density of weak stress bond formed by Si and -H or -OH[10] of soft SiO_2 is greater than that of hard sample, due to the introduction of HCl. The number of pairs in the soft sample coming from weak stress bonds broken by the gamma rays, is therefore much larger than that in hard oxide. Hence the difference between hard and soft oxides in spectra of Si 2p(B.E. 103.4 eV) appears. Ionizing radiation also breaks up the weak stress bond corresponding to SiO_x (B.E. 101.5 eV), that is not an entirely insulating film, such oxygen atoms of the soft sample can not compete with -H or -OH in making bond with Si, so they exist as surplus oxygen form after irradiation, while the broken Si-H and Si-OH corresponding to SiO_x recombine. The spectrum changes of surplus oxygen and Si 2p in transitional state are thus very small in soft oxide. Si recombining with -H or -OH probability belonging to broken SiO_x of hard sample is smaller than that of soft, as a result the proportion of transitional state Si drops. It is one of the reasons that the hard process can improve the resistance of bearing ionizing radiation of device.

3.2 The influence of bias field observed from Fig.3, 4

a. Si 2p XPS spectra of silica state (103.4 eV) indicate that the peaks of soft and hard oxides irradiated under free bias field do not shift remarkablely, at the same time the peak area changes slightly, while the peak positions of hard and soft irradiated under +1 MV/cm move to high energy.

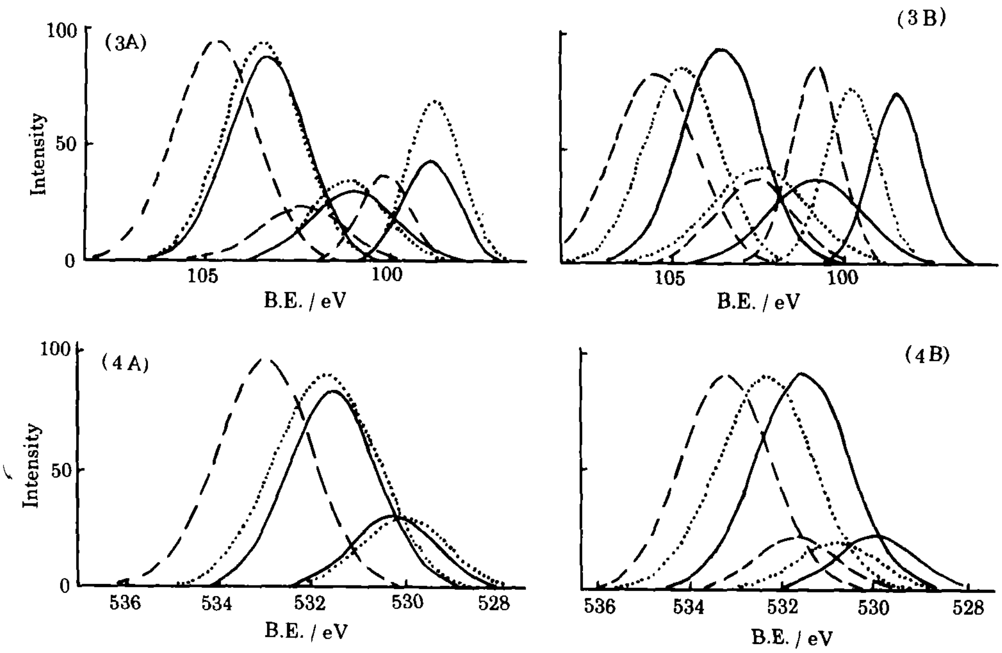

Fig.3,4 Si 2p (3) and O 2s (4) XPS spectra of the samples under the different bias fields

A: Soft oxides B: Hard oxides

— 0 Gy (Si) --- 50 kGy (Si), +1 MV/cm ··· 50 kGy (Si), 0 MV/cm

b. Si 2p XPS spectra of SiO_x state (101.5 eV) show that the peaks of soft and hard samples irradiated under +1 MV/cm move to high energy, meanwhile the percentage of this peak area for the soft is declining, for the hard is unchanged, both peak location and its percentages of the two kinds of oxides irradiated under free bias field do not vary.

c. The intensity of O 1s (531.4 eV) adds with increasing intensity of bias field in hard sample, whereas it changes very small in soft oxide. If we irradiate both hard and soft Si–SiO_2 under positive bias field, the place of binding energy corresponding to negative two–valence oxygen shifts to high energy. The concentration of surplus oxygen in hard oxide vigorously depends upon the bias field, for we can observe the surplus oxygen in the hard before irradiation. However; we can not observe it in such Si–SiO_2 after irradiation in +1 MV/cm. The XPS spectra of surplus oxygen state are independent of the bias field in soft sample.

Along the surface of SiO_2 positive bias field sweeps off electron produced by gamma rays in Si-SiO_2 structure, and the density of surface state rises simultaneously[11,12]. But under free bias field there is no such effect.

4 CONCLUSIONS

Electron-hole pairs in Si-SiO_2 system are produced by breaking up both weak stress bonds belonging to SiO_2 state (B.E. 103.4 eV) and SiO_x ($x = 1.1$) state (B.E. 101.5 eV). The action of surplus oxygen is that it promotes establishment of bond with high oxidic state[13] during the course of electron-hole pair recombination. The density of weak stress bonds consisting of Si and -H or -OH increases because of the introduction of HCl and Si-SiO_2 system unannealed during soft process, which makes trap charge and density of interfacial state increase greatly after irradiation. In contrast to soft process, hard oxidation process restrains the growth of weak stress bonds so that the performance change of Si-SiO_2 system is small in irradiation environment.

XPS spectra at the Si-SiO_2 interface indicate that the damages by irradiation dose is greater than that by irradiation bias field under the same conditions of device.

REFERENCES

1 Wang Shouwe. Research and development of semiconductor device. Beijing: Sinica Publishing House, 1988; 36
2 Zhong Cun Shengwu. Surface physics. Beijing: Scholastic Book and Journal Publishing Hourse, 1989; 1
3 Stahlbush R E, Carlosand W E, Prokes S M. IEEE Trans Nucl Sci, 1987; NS-34(6): 1680
4 Chihiro Itoh, Toshio Suzuki, Noriaki Itoh. Phys Rev, 1990; B41(6): 3794
5 Grunthaner F J, Lewis B F, Zamini N. IEEE Trans Nucl Sci, 1980; NS-27(6): 1640
6 Liu Changshi, Zhao Yuanfu, Liu Fen. Nuclear Techniques (in Chinese), 1992; 15(9):554
7 Packwood R H, Remond G, Holloway P H. Surface and Interface Analysis, 1988; 11:127
8 Nagasima N, Enari H. Jap J Appl Phys, 1971; 10(4):441
9 Sugano T, Hoh K. Jap J Appl Phys, 1968; 7(7):715
10 Grunthaner F J, Maserjian J. IEEE Trans Nucl Sci, 1977; NS-24(6):2108
11 Liu Changshi, We Qinzhi, Zhang Lingshan. Microelectronics and Computer (in Chinese), 1989; 6(12):5
12 Song Qinqi, Microelectronics and Computer (in Chinese), 1989; 6(12):11
13 Zhong Cun Shengwu. Surface physics. Beijing: Scholastic Book and Journal Publishing House, 1989; 97