Available online at www.sciencedirect.com
SCIENCE DIRECT
Vacuum 75 (2004) 51–55
VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY
www.elsevier.com/locate/vacuum

Plasmons in double interfaces system of $Si_3N_4/SiO_2/Si$ irradiated by ^{60}Co

Liu Changshi*

Department of Physics, Shaoxing College of Arts and Sciences, Shaoxing University, Shaoxing, Zhejiang 312000, PR China

Received 12 October 2003; received in revised form 2 December 2003; accepted 29 December 2003

Abstract

The first level plasmons of Si in the pure Si state, in the SiO_2 state and in the Si_3N_4 state (corresponding to bonding energy 116.95, 122.0 and 127.0 eV) were investigated directly with X-ray photoelectron spectroscopy before and after ^{60}Co radiation. The experimental results demonstrate that there existed two interfaces, one consisted of plasmons of Si in the Si_3N_4 and SiO_2 states, while another was made of plasmons of Si in the pure Si state and in the SiO_2 state. When the Si_3N_4–SiO_2–Si samples were irradiated by ^{60}Co, the interface at Si_3N_4/SiO_2 was extended and at the same time the center of this interface moved towards the surface of Si_3N_4. The concentration of plasmon for silicon in the SiO_2 state is decreased at the SiO_2–Si interface, and the effects of radiation bias field on plasmons in the SiO_2–Si interface are observable. Finally, the mechanism of experimental results is analyzed by the quantum effect of plasmon excited by the photoelectron.

Keywords: Plasmons; Si_3N_4; SiO_2–Si; Dosage; Bias field

1. Introduction

The SiO_2/Si interface has been extensively studied in the past years because of its influence on the performance of metal–oxide–semiconductor devices, especially for metal–oxide–semiconductor-very large-scale integrated (VLSI) circuits. The wear out and breakdown of thick SiO_2 film has been extensively researched. Several models involving local hole trapping and oxide field buildup during Fowler–Nordheim electron tunneling have been proposed to explain oxide breakdown [1,2]. A lower effective barrier height for electrons and the image charge effect are caused by positive oxide charge (hole trapping) and tunneling path of Fowler–Nordheim reduced [2,3]. Because of lack of a physics-based model, there has been persistent concern over the severity and even the existence of positive oxide charge buildup, since the power supply voltage decreased from 5 to 3.4 V.

Several mechanisms were presented to explain charge generation by ionic radiation [3–6]. For thick oxides the impact ionization model of electron–hole pair generated in the oxide bulk shows reasonable agreement with experiment. However, the generation mechanism of the radiation damage induced by ^{60}Co in double interfaces system of $Si_3N_4/SiO_2/Si$ has not yet been studied, especially, using some ways to detect plasmon. Attempts to detect the surface and bulk plasmons

*Corresponding author. Tel.: +86 0575 806 7065.
E-mail address: liucs4976@sohu.com (L. Changshi).

0042-207X/$ - see front matter
doi:10.1016/j.vacuum.2003.12.162

can be on indirect observations, such electron-energy loss, radioactive decay of the plasmons, or measurement of dI^2/dV^2 [7]. It is X-ray photoelectron spectroscopy (XPS) that can give signal of the surface, interface and bulk plasmons directly. In this study, double interfaces system of $Si_3N_4/SiO_2/Si$ sample irradiated by ^{60}Co was measured by the XPS; focus is on the changes of the interfacial plasmons created by radiation condition. The experimental results demonstrate that there existed such variance, and the results are explained by the quantum effect of plasmons excited by photoelectron.

2. Experimental details

The structure of the $Si_3N_4/SiO_2/Si$ is shown in Fig. 1. The samples utilized in this work were in the form of silicon wafer (n-type ρ 6–9 Ω/cm) with surface orientation $\langle 1\,0\,0 \rangle$. Oxide was grown in dry O_2 at 1273 K to a thickness of 21 nm firstly, then 40 nm silicon nitride layer was deposited on top of the oxide by a low pressure CVD and annealed in situ in at mix gas of oxygen and hydrogen (O_2+H_2) at 1173 K for 30 min resulting in $Si_3N_4/SiO_2/Si$ sample. Because the thermal expansion coefficients of SiO_2, Si and Si_3N_4 are different, annealing at high temperatures may create some interfacial defects. In order to keep the level of interfacial defects was the same for all samples before radiation, all samples were taken from one $Si_3N_4/SiO_2/Si$ chip and were p-channel transistors with metal Al gates. In such case, however, the experimental results would not be affected to follow comparing of among the spectra of plasmon in the form of XPS. The thinner oxide is, the lower sensitive to ionization radiation of

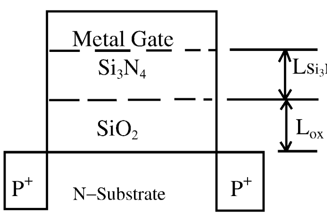

Fig. 1. The structure of the Si_3N_4–SiO_2–Si measured in this work.

SiO_2/S interface will be [8,9]. According to this reason, here the oxide was grown in thin form.

The γ-irradiation was performed at room temperature with a ^{60}Co source of an energy of 1.25 MeV, and the dosage of radiation ranged from 0 to 10^4 Gy (Si). The bias fields during irradiation were 0 and -1 MV/cm. In order to make targets appropriate for XPS measurement, hydrogen peroxide and sulphuric acid solution was employed to remove the Al layer of Ohmic contact before inserting the $Si_3N_4/SiO_2/Si$ samples into the XPS cavity.

XPS measurements were carried out via a KRATOS XSAM800 electron spectrometer. An Ar^+ ion beam was used to etch the Si_3N_4 and SiO_2 films. There might be two effects of sputtering. Firstly, when sputtering, there was always the possibility of different sputtering rates of the elements, another is that atoms might be pushed down into deeper layers of the sample and atoms from the lower layers of the sample might be transported to the upper layers of the sample. In order to overcome the effects above on experimental results, each sample was etched by a fixed ion beam parameters of Ar^+, i.e., at energy of 4 keV, identical etching time and beam current to keep to the same extent of the two effects upon each sample. In such case, however, the experimental results would not be affected to follow comparing of among the XPS spectra. The vacuum during the measurement was less than 1.3×10^{-6} Pa. The samples were excited by 1486.6 eV Al K_a X-rays. The sweep range was 20 eV for both Si_3N_4 and SiO_2, and other parameters of measurement, such as reg, step, dwell and scan numbers were the same for every measurement. Each spectrum was calibrated to C at bonding energy (BE) 285 eV, and every peak was stimulated from original spectrum by code DS300X Data System. BEs have been used as index of the plasmons [10,11].

3. Results and discussion

In order to voice interfaces objectively, relative intensity is accepted. Fig. 2 gives plots of the etch time-normalized area before and after radiation

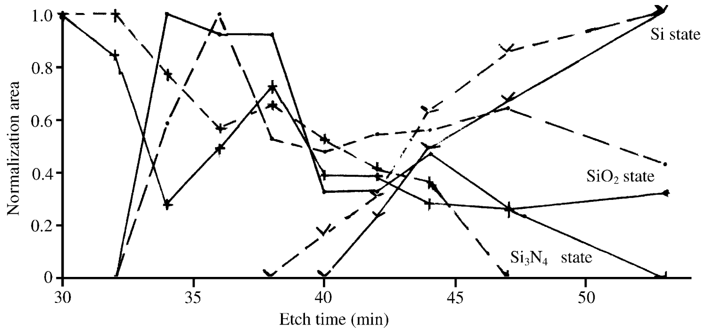

Fig. 2. Profiles of the etch time—normalized area for plasmon in the $Si_3N_4/SiO_2/Si$ before and after radiation. The curves - - - and —— refer to results of plasmon from the $Si_3N_4/SiO_2/Si$ samples unexposed and exposed to 10^4 Gy (Si) of ^{60}Co gamma radiation at -1 MV/cm bias field, respectively. The direction of normalized areas for plasmons in the pure Si state ($^\vee$ BE 116.95 eV), in the Si_3N_4 state (+ BE 127 eV) and in the SiO_2 state(● BE 122 eV) are area at the Si substrate, area at the surface of Si_3N_4 and the peak with maximal area of plasmon in the SiO_2 state.

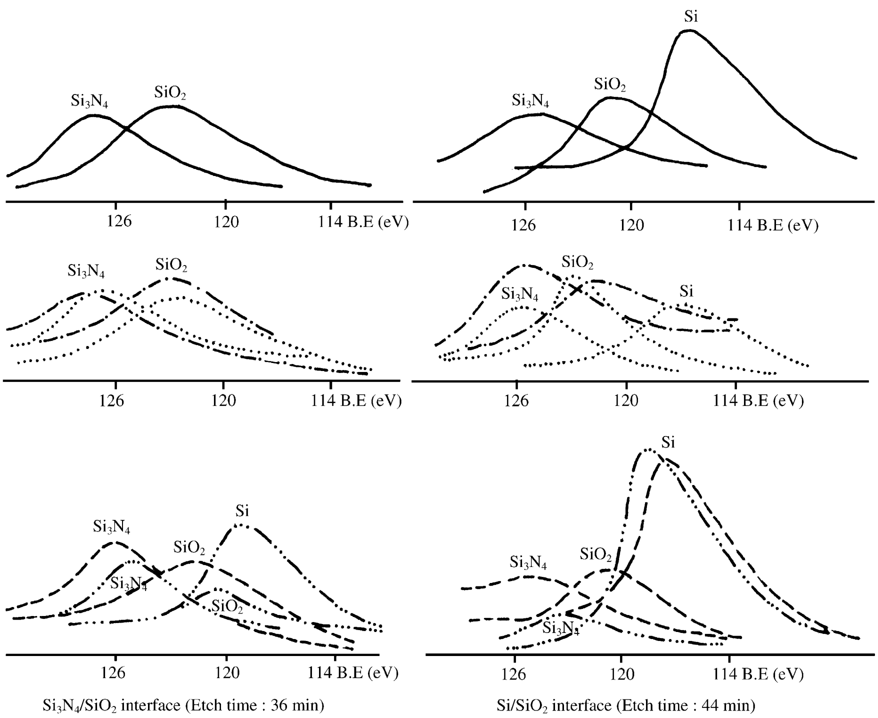

Fig. 3. The plasmon peaks fitted from original spectra at the Si_3N_4/SiO_2 and SiO_2/Si interfaces irradiated in different radiant environment. The curves expressed by ——, ● ● ● ●, —●—●— and — — — refer to samples exposed to $0, 10^2, 10^3$ and 10^4 Gy (Si) of ^{60}Co gamma radiation at -1 MV/cm bias field,— ● ● ● — ● ● ● — is the sample exposed to 10^4 Gy (Si) of ^{60}Co gamma radiation at 0 MV/cm bias field (before being referenced to C).

[10]. The direction of normalized areas for plasmons in the pure Si state (BE 116.95 eV), in the Si_3N_4 state (BE 127 eV) and in the SiO_2 state (BE 122 eV) are area at the Si substrate, area at the surface of Si_3N_4 and the peak with maximal area of plasmon in the SiO_2 state. Because the sputter

time corresponds to the depth from the surface of Si_3N_4 to the substrate Si, Fig. 2 also shows the profiles of plasmons in the $Si_3N_4/SiO_2/Si$. It can be observed in Fig. 2 as expected that (1) there exists an interface of plasmons made of Si_3N_4 and SiO_2, and another interfaces of plasmons consisted of SiO_2 and Si. Furthermore, if the sputtering effect level of Ar^+ ion beam on Si_3N_4 is considered to be similarity to that on SiO_2, the thickness of the interface Si_3N_4–SiO_2 is about the same that of SiO_2–Si. (2) The interface of plasmons at Si_3N_4/SiO_2 is extended, meanwhile, the center of this interface moved towards the surface of Si_3N_4 by the actions of radiation. Unlike previous work [12], the interface of plasmons at SiO_2/Si is not changed.

Fig. 3 displays the differences in plasmons of the double interface samples in the XPS spectra before and after radiation. The figure shows that the feature of plasmon labeled "Si" in the SiO_2 state located at the interface SiO_2–Si was decreased when the radiation dose was up to 10^4 GY (Si) at the bias field of -1 MV/cm, obviously, and the plasmon of Si in the SiO_2 state reduced greatly due to the bias-free field at this radiation dose.

To explain these results, the photoelectron energy loss in Si_3N_4 and SiO_2 is discussed by using Fig. 4. When a beam of photons is brought to bear on a target, energy is deposited in the materials as kinetic energy and the potential energy of the atoms ionized and excited. The energy of photoelectron generated by ^{60}Co is above 80 eV at least. The photoelectron of this kind can slightly penetrate into the Si_3N_4 and SiO_2 because the inelastic mean free path (IMFP) of photoelectron is around 0.5 nm. Then, photoelectron excite surface and interfacial plasmons as well as secondary electrons, which can excite bulk plasmon by the "spur" process [13]. This energy-loss process is called the "blob" process. The characteristic length of the reaction volume in which plasmons are excited by electron is known as radius d_r. The d_r for electron above 80 eV is above 10 nm, and called the Onsager radius.

It is known that only the photoelectrons with energy equal to $nh\nu_s$, $mh\nu_i$ or $kh\nu_b$ can lose their energy by exciting surface plasmons, interfacial plasmons and bulk plasmons, respectively. Here,

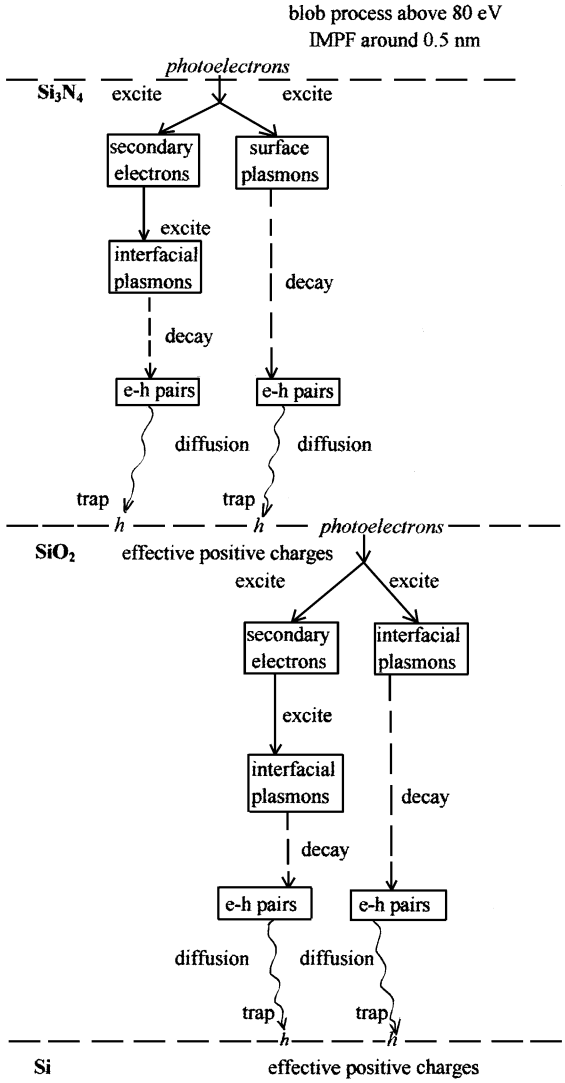

Fig. 4. Photoelectron energy-loss theory in Si_3N_4/SiO_2. Blob process: Photoelectrons above 80 eV can slightly penetrate into the Si_3N_4 and SiO_2 because the IMFP is around 0.5 nm. Then, photoelectrons excite surface plasmons, interfacial plasmons as well as secondary electrons, which can create interfacial plasmons by the spur process. The d_r for electrons above 80 eV is about 10 nm.

n, m and k are integers, and $h\nu_s$, $h\nu_i$ and $h\nu_b$ are the quantum creation energies of surface plasmon, interfacial plasmon and bulk plasmon, respectively. The quantum absorption energy can be calculated theoretically [14,15]. The path to create plasmon of Si in the SiO_2 state is the shortest in samples, and the yield of photo-induced electrons is 10^{-4} order. Furthermore, the direction of acceleration for photoelectron due to $-1\,MV/cm$ bias field is from the surface of Si_3N_4 to Si substrate, but the oxygen atoms either couple with N or do Si in SiO_2 layer. The intensity fraction of plasmon for Si in SiO_2 state may be very small generated by photoelectrons and secondary electrons due to reasons above, parallely, therefore, the intensity percentage of plasmon for Si in SiO_2 state had not been changed until the dose was up to 10^4 GY (Si). Most photoelectrons create plasmons either in the layer of Si_3N_4 or in the layer of Si and are without loss energy in the layer of SiO_2. If the dose is up to 10^4 GY (Si) with higher dose rate and acceleration field, which looks like pumping effect, thus, there is the smallest intensity fraction of plasmon corresponding to SiO_2 in the XPS spectra. The feature labeled plasmons produced by ^{60}Co at bias-free field is substantially more intense of Si in the pure Si state. The possible reason is that the energy of photoelectron excited by gamma ray at bias-free field may be the lowest in this experiment, as well as the quantum creation energy of bulk plasmon $h\nu_b$, and these make choice absorption easy. When one pay attention to the change of profile, the photoelectrons transmitted Si_3N_4 and the layer of this medium is longer than that of SiO_2, this is one reason why the interface of plasmons at Si_3N_4/SiO_2 is extended and the center of this interface moved towards the surface of Si_3N_4, or this result suggests that the existion of the Si_3N_4 layer replaced the main area of plasmons generated from the SiO_2 layer into Si_3N_4 layer.

4. Conclusions

The plasmons of the double interfaces system of $Si_3N_4/SiO_2/Si$ have been analyzed before and after radiation, successfully. The plasmons are excited in zone of Si_3N_4 and Si mainly, this is very unlike the plasmons produced by gamma rays in the interface of SiO_2/Si. The bias field is still very important factor among radiation environment. Experimental results also demonstrated that in order to reduce the degeneration of MOS generated by ionic radiation, the introduction of Si_3N_4 layer is necessary because it transferred the main area to crate plasmons from SiO_2/Si interface into Si_3N_4–SiO_2 interface.

References

[1] Chen IC, Holland S, Hu C. IEEE Trans Electron Devices 1985;32:413.
[2] Holland S, Chen IC, Ma TP, Hu C. IEEE Electron Device Lett 1984;EDL-5:302.
[3] Chen CF, Wu CY. Solid-State Electron 1986;29:1059.
[4] Fischetti MV, Weinberg ZA, Calise JA. J Appl Phys 1985;57:418.
[5] Fischetti MV. Insulating films on semiconductors. In: Simonne JJ, editor. Amsterdam: North-Holland; 1986. p. 186.
[6] Fischetti MV. Phys Rev B 1985;31:2099.
[7] Jong-Hyun Kim, Julian J. Sanchez, Thomas A. DeMassa, et al. J Appl Phys 1998;84:1430.
[8] Grunthaner FJ, et al. Phys Rev Lett 1979;43:1683.
[9] Grunthaner FJ, et al. IEEE Trans Nucl Sci NS-29 1982;6:462.
[10] Kittel C. Introduction to solid state physics, 7th ed. Singapore: Wiley; (ASIA) Pte. Ltd.; 1996. 326pp.
[11] Wang Jianqi, Wu Wenhui, Feng Damin. Introduction to electronic energy spectroscopy (XPS/XAES/UPS). Beijing: Publishing House of National Defense Industry; 1992. p. 78–9 [in Chinese].
[12] Liu Changshi. Nucl Sci Technol 1999;10(1):1.
[13] Takashi Yunogami, Tatsumi Mizutani. J Appl Phys 1993;73:8184.
[14] Moreau P, Brun N, Colliex C, et al. Phys Rev B 1997;56:6774.
[15] Hovel H, Fritz S, Kreibig U, et al. Phys Rev B 1993;48:18178.