Charge trapping and charge compensation during Auger electron spectroscopy on SiO_2

Hansheng Guo[a)]
Department of Materials Science and Engineering, Beijing Polytechnic University, 100022 Beijing, People's Republic of China

W. Maus-Friedrichs and V. Kempter
Physikalisches Institut der Technischen Universität Clausthal, Leibnizstrasse 4, D-38678, Clausthal-Zellerfeld, Germany

(Received 8 June 1998; accepted for publication 3 May 1999)

It is well known that radiolysis, induced by the electron bombardment, leads to different defects in SiO_2, but little is known about the trapping behavior of these defects. In this article, the charging behavior and the depth profiles of the irradiation damage introduced by electron bombardment are studied with Auger electron spectroscopy (AES). For charge reduction an environmental AES using O_2 (up to 8×10^{-8} Torr) and specimen heating are applied. In environmental AES, a strong charge reduction is observed, and the importance of the environment for charge compensation reveals a correlation with electron stimulated desorption. By heating the sample, a strong charge reduction takes place above 500 °C; complete charge compensation can be expected by heating the sample above 700 °C in an O_2 environment of 5×10^{-8} Torr. We suggest that E' centers, nonbridging oxygen hole centers, and peroxy radicals, are responsible for the efficient trapping of electrons. The observed discharging is believed to be related to the annealing of the defects. © *1999 American Institute of Physics.* [S0021-8979(99)01616-3]

I. INTRODUCTION

Electron trapping under electron bombardment has been observed in single crystals of quartz, amorphous SiO_2 and metal–oxide–semiconductor (MOS) capacitors.[1,2] The cross section for electron stimulated desorption (ESD) of SiO_2 is 1.5×10^{-20} cm^2,[3] the reduction of the surface, subjected to electron radiation at an energy of 2 keV and a current density of 10 mA/cm^2, can be significant within 1 min.[4] Low energy electron irradiation cannot produce defects by the direct momentum transfer, instead the mechanism of the defect formation is assumed to be radiolytic whereby an atom is displaced in the course of electronic excitations, such as self-trapped excitons.[5] In radiated SiO_2 the well characterized defects by electron spin resonance (ESR) include E' center ($\equiv$Si$^\cdot$Si$\equiv$), dry and wet nonbridging oxygen hole center (NBOHC:$\equiv$Si–O$^\cdot$, and peroxy radical (PR:$\equiv$Si–O–O$^\cdot$).[6] For these defects with unpaired spins, the E' center is positively charged, and NBO and PR are electrically neutral. If the defects trap electrons, i.e., states with paired spins are formed, they become ESR invisible,[6] thus little is known about their charging behavior.

Carroll, Doering, and Xing-Skiba investigated thermionic emission of a α-quartz sample which had been exposed to different doses of an electron beam of energies between 2 and 4 keV.[7] They had assigned the peaks to the emission from wet NBOHC or OH species and from oxygen vacancies in the surface. Vigouroux *et al.*[1] concluded that the E' precursor may serve as electron trap, but denied that NBO and PR can trap electrons. Aitken, Young, and Pan identified four different neutral trap centers in dry oxidized MOS after exposure to electrons with an energy of 25 keV and fluxes between 2.5×10^{-5} and 1×10^{-8} C/cm^2.[2] A significant thermal detrapping for captured electrons demands an annealing temperature beyond 550 °C.

We have introduced environmental Auger electron spectroscopy (AES) using O_2 for the analysis of oxides.[8] It has been shown that a satisfactory compensation of all the irradiated effects on Al_2O_3 (charging phenomena, ESD, and contamination of the surface from residual gas) is achieved in 5×10^{-8} Torr O_2. ESD on SiO_2 can be reduced significantly in the environmental AES, although charge compensation can be achieved only for lower primary energies.

For a better understanding of these differences, the charging behavior of SiO_2 and the depth profiles of the irradiation damage is studied in this article. In addition, the efficiency of the charge compensation of environmental AES using O_2 (up to 8×10^{-8} Torr) and the annealing behavior of the charge with and without O_2 exposure is examined. The nature of thermal annealing and the efficiency of the environmental AES offer a mean for differentiation of the defect centers and for examining their special distribution.

II. EXPERIMENT

The experiment is performed in a scanning Auger electron microprobe utilizing a cylindrical mirror analyzer with an integrated electron gun. The base pressure in the analysis chamber is better than 5×10^{-10} Torr. The system has been described in detail previously.[8,9] The integrated electron gun is applied for sample excitation, as well as for damaging and

[a)]Author to whom correspondence should be addressed; electronic mail: weipengl@bjpu.edu.cn

 © 1999 American Institute of Physics

Downloaded 22 Dec 2004 to 139.174.155.153. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

TABLE I. The primary parameters used in this work.

Primary energies	E_p [keV]	1	2	3	5	8
	$\alpha=0°$	0.42	0.64	1.24	3.17	79.62
Primary current density	$\alpha=30°$	0.37	0.55	1.08	2.76	68.95
$J_p[10^{-2}\text{A/cm}^2]$	$\alpha=60°$	0.22	0.32	0.62	1.59	39.80

charging the sample. The primary current density at the applied angles of incidence α (with respect to the specimen normal) varies with the primary energy (E_p) as indicated in Table I.

For charge compensation of the sample, an O_2 environment below 8×10^{-8} Torr can be supplied. Environmental AES means that the specimen under study is in a controlled gaseous environment. In O_2 environmental AES below 8×10^{-8} Torr, the reoxidation of the reduced surface of the oxide samples is the dominating process for charge reduction.[8]

The annealing behavior of the charging phenomena in SiO_2 samples with and without O_2 exposure is investigated. Due to the poor thermo-conductivity of SiO_2, the measured temperature can be underestimated seriously. Throughout this article the temperature of the sample support is given.

The sample is a pure quartz glass (a-SiO_2) with dimensions 10 mm×10 mm×1 mm. It was cleaned in acetone in an ultrasonic bath, then rinsed with distilled water. After transfer into the analysis chamber the sample was heated to 600 °C for 30 min to eliminate water. Before measurement the sample was further cleaned with Ar^+ sputtering at 1 keV until any carbon contamination in the AES spectra had disappeared.

III. RESULTS

In previous studies it was found that among the oxides Al_2O_3, YS–ZrO_2, and SiO_2, SiO_2 suffers the strongest charging under the same primary parameters;[8] at an incidence angle of 30° and a primary energy of 2 keV the sample charges immediately. The series spectra in Fig. 1 is acquired at the primary energy of 1.5 keV and $\alpha=30°$. The irradiation time is given for each spectrum. After 1 min of exposure the reduction of the surface is measurable, which is indicated by the increasing ''element'' peak Si_{el} in the Si LVV transition. The sample begins to charge within 1.5 h, and the maximal charge potential amounts to 300 eV after a radiation period of 12 h. The charge potential is measured from the energy shift of the Auger peaks (U_C). Table II gives an overview of the charging behavior (the charge potential after a certain irradiation time and the maximal charge potential U_{CM}) for the primary energies from 1 through 8 keV at 30° and 60° incidence angles, respectively. Although at the same primary energy, the charging is less serious at incidence angle of 60° compared to 30° incidence, the reduction of the surface is more significant. It is obvious that a complete and reliable Auger spectrum cannot be obtained with conventional AES.

SiO_2 charging can be reduced with an O_2 environment. Figure 2 shows the spectra obtained in an O_2 atmosphere of 5×10^{-8} Torr, but the primary parameters are the same as that in Fig. 1. The irradiation time is given for each spectrum. The sample in 5×10^{-8} Torr O_2 remains uncharged for at least 12 h, while at the same time ESD of surface oxygen is strongly reduced compared with in UHV. The maximal charge potential measured at different O_2 pressure is given in Fig. 3. Typically, a strong reduction of the charge is observed up to 2×10^{-8} Torr O_2; at 30° incidence the maximal charge potential at the primary energies 2 and 3 keV in 5×10^{-8} Torr O_2 can be reduced by ~650 and 800 eV, respectively, a comparison with in UHV. An O_2 environment during AES has also the effect to prevent the surface from carbon contamination by residual gases, such as carbon oxides. In fact, when the surface is contaminated with carbon initially, the adsorbed carbon species can be desorbed under electron bombardment in an O_2 atmosphere. Obviously the carbon species is removed by the oxygen exposure, possibly by formation of carbon oxides, which desorb.

Figure 4(a) shows the spectra obtained in UHV at electron energy of 3 keV at different temperatures of the sample

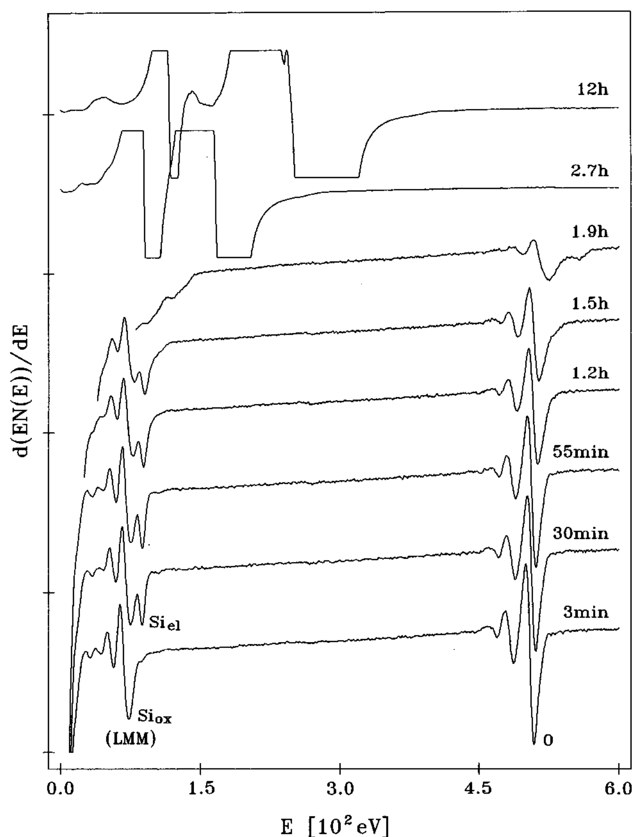

FIG. 1. A series of spectra showing the oxygen depletion and the charging-up under a continuous electron bombardment, the irradiation time is given for each spectrum. Primary electron beam: energy 1.5 keV; 30° incidence.

Downloaded 22 Dec 2004 to 139.174.155.153. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

TABLE II. The charging behavior of SiO_2 under electron radiation.

α	E_p [keV]	1	3	5	8
30°	Charging-up	250 eV/10 h	600 eV/10 m	1000/5 s	2500 eV/3 s
	U_{CM} [eV]	400	1600	$\geqslant$2500	>2500
60°	U_{CM} [eV]	0	10	$\geqslant$500	>1800

support. Charges can be reduced by specimen heating, which becomes more significant with increasing temperature beyond 500 °C. An additional O_2 exposure of 5×10^{-8} Torr to the specimen heating reduces the charge potential ~200 eV further, as shown in Fig. 4(b). Therefore, charge compensation can be expected by specimen heating of above 700 °C with this O_2 exposure.

Figure 5(a) shows depth profiles of two different spots which had been bombarded by 5 keV electrons for 45 h in UHV and in 1×10^{-4} Torr Ar. Figure 5(b) presents that of another two spots which had been bombarded by 3 keV electrons for 39 h. The Ar^+ sputter rate (2 keV and 2.5×10^{-5} A/cm^2) is ~46 Å/min.[10] The ordinate denotes the oxygen deficiency, characterized by the ratio of ''element'' peak Si_{el} at 92 eV and ''oxide'' peak Si_{ox} at 76 eV in the Si LVV spectrum. The maximal oxygen deficiency is not located on the surface, as has been interpreted by Calliari as oxygen segregation induced by irradiation.[11] The Si_{el}/Si_{ox} ratio drops at the primary energy 5 keV after sputtering for 45 min to 0.9 and at 3 keV for 30 min to 0.8. If the preferential sputtering and ESD of oxygen is taken into consideration, assumed by saturation Si_{el}/Si_{ox}~0.9 for E_p=5 keV and ~0.8 for E_p=3 keV, the oxygen deficiency for 5 keV electron irradiation stretches 210 nm into the material, and 140 nm for the 3 keV electron irradiation.

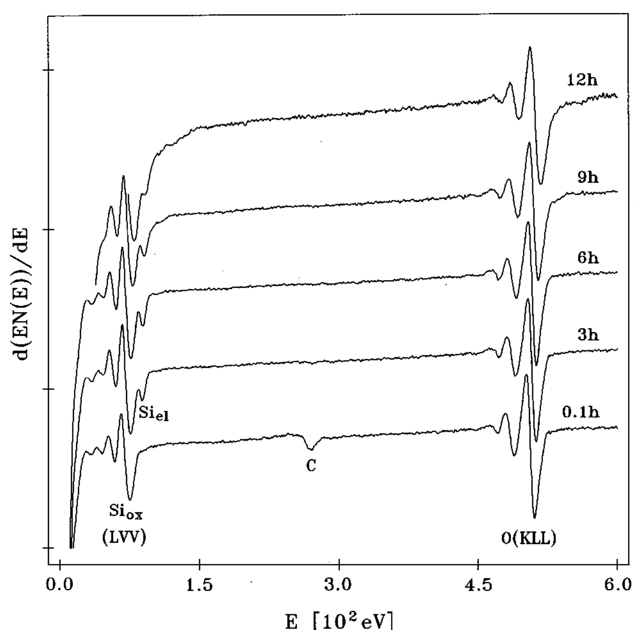

FIG. 2. The spectra acquired at 1.5 keV and 30° (in 5×10^{-8} Torr O_2). The irradiation time is given for each spectrum.

IV. DISCUSSION

Intrinsic and extrinsic defects, as well as the irradiation damage are possible candidates for traps in the SiO_2 sample. It is known that several atomic impurities may be incorporated into a-SiO_2 during its growth. For example, sodium and aluminum are well known possible impurities in a-SiO_2, and both introduce electron traps.[12,13] The measured sample is pure a-SiO_2; none of these impurities had been detected in AES, thus, they cannot be responsible for the strong charging. OH groups give other possible electron traps; they can be incorporated into SiO_2 by the diffusion of H after a long exposure to air.[14]

The pair generation of E' centers and NBOHCs from intrinsic SiO bonds is suggested to occur along the trajectories of the primary electrons,[5] the E' centers react in turn with interstitially existing molecular oxygen to form peroxy radicals.[15] Induced by ESD, a decrease of the oxide peak and an increase of the element peak in the Si LVV spectrum can be noticed in Fig. 1. It is obvious that the oxygen desorption is the precursor process of the surface charging. At tilt incidence, more energy of the primary electrons is dissipated in the top surface of the sample,[16] where ESD of oxygen takes place. In this instance, the charging phenomena is superficial, which in turn can be efficiently compensated by reoxidation of the reduced surface in the presence of the O_2 environment. At steep incidence the primary electrons dissipated more energy deep inside the sample,[16] whereby more defects, such as E' centers, NBOHCs, and PRs, and then charges are induced, which are not efficiently compensated by the O_2 environment.

Figure 5 shows that after long electron radiation the oxygen deficiency stretches to a depth comparable with the pen-

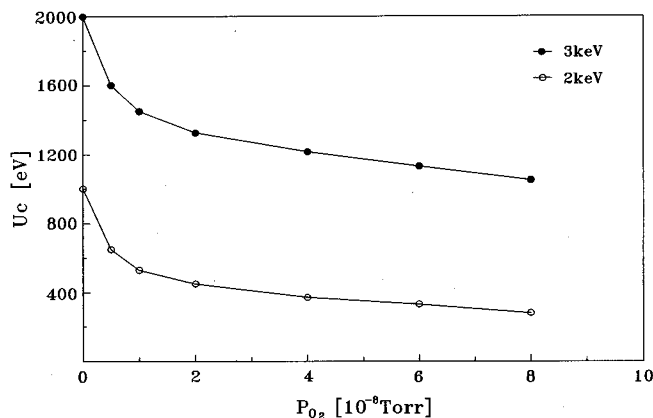

FIG. 3. The saturation charge potential at the primary energy 2 and 3 keV in the O_2 environment from 0 to 8×10^{-8} Torr (each pressure was kept for 6 h, α=30°).

Downloaded 22 Dec 2004 to 139.174.155.153. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

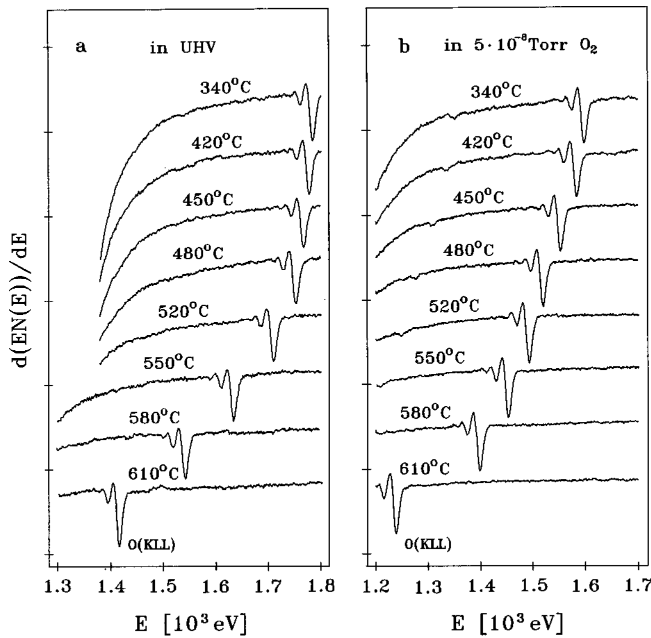

FIG. 4. The charge potentials at different temperatures on sample support (a) in UHV and (b) in 5×10^{-8} Torr O_2 (E_p=3 keV and α=30°).

etration depth of the primary electrons. By comparison with the depth profile on Al_2O_3, on which the oxygen deficiency extends 25 nm into the bulk after a lasting electron radiation,[16] we conclude that the oxygen deficiency in SiO_2 beyond 25 nm cannot result from the diffusion or the segregation of the defects. Therefore, a direct irradiation damage in SiO_2 from the radiolysis must be taken into account. The defects, such as E' center, NBOHC, PR, and Frenkel–Pair, can be induced along the trajectories of the primary electrons. During sputtering these defects are exposed to the surface layer by layer, with a distribution corresponding to the energy dissipation of the primary electrons.[16] With the weak bonds in PRs (≡Si–O–O˙) the oxygen desorbs readily under the electron or ion beam bombardment, thus, one sees a higher oxygen deficiency in the penetration depth of the primary electrons in comparison with the saturation value after the irradiated layer has been sputtered.

The defect centers introduce energy levels into the band gap,[17,18] as shown schematically in Fig. 6. The E' center denoted a relaxed and single positively charged oxygen vacancy. In this defect the lower energy level is singly occupied; the upper level, lying 2.5 eV below the minimum of the conduction band, is empty.[19] It is suggested that the ''neutral'' oxygen vacancies (≡Si–Si≡) were formed from E' centers after trapping an electron.[20,21] Actually, because of the covalence nature of SiO_2 the neutral oxygen vacancies (occupied by two electrons) are effectively charged negatively.[22]

The NBOHC has two $p\pi$ states. One of them offers a local level in the band gap which is singly occupied in the neutral NBO. This level can be occupied twice, i.e., be charged negatively.[12]

For the PR the deep lying π^* level is singly occupied, therefore, PR is again a trapping center for electrons. The charging capability of the PR can be visualized as follows:

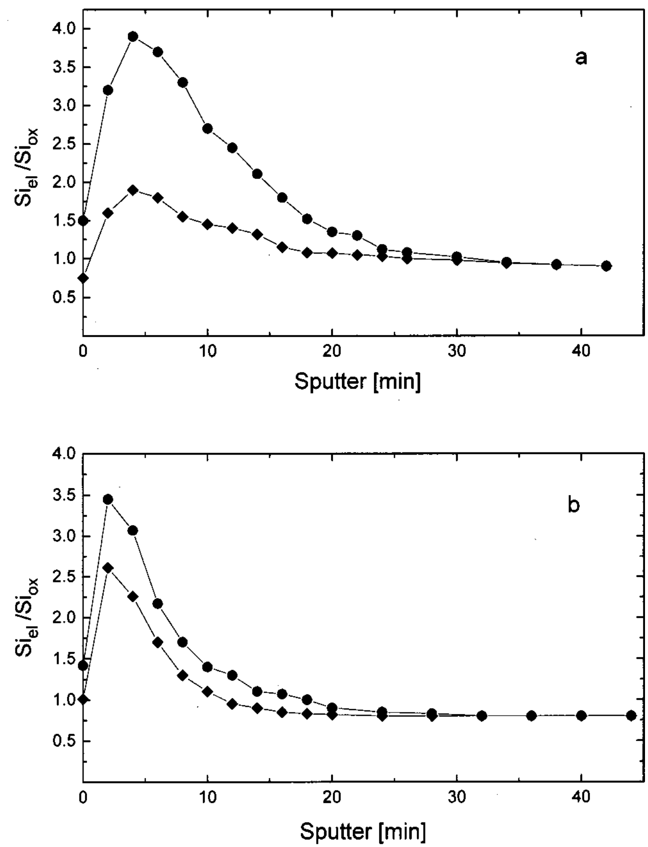

FIG. 5. Depth profiles of the spots on the surface irradiated (a) with 5 keV electron for 45 h and (b) with 3 keV electron for 39 h (●: in UHV; ◆: in 1×10^{-4} Torr Ar).

The two oxygen atoms in the PR have a bond length comparable to that of free oxygen molecule-ion;[23] because of the partial ionic bond of SiO_2 the neutral PR possess a net charge ~−0.5 e.[24,25] It has been found that O_2^{2-} is a stable unit at the Ag-metal surface, which has a net charge ~−1.4 e.[26] Accordingly, the negatively charged PR with an effective charge of −1.4 e is energetically stable.

SiO_2 has a specific resistance at room temperature of 1×10^{16} Ω cm.[27] Heating to 185 °C reduces this value to 5×10^{15} Ω cm.[28] Thus, by heating to several hundred degrees centigrade, one cannot expect that the specific resistance can be reduced in a way so that its charging can be avoided completely. However, the defects induced by irradiation can be annealed by appropriate heating, simultaneously, dis-

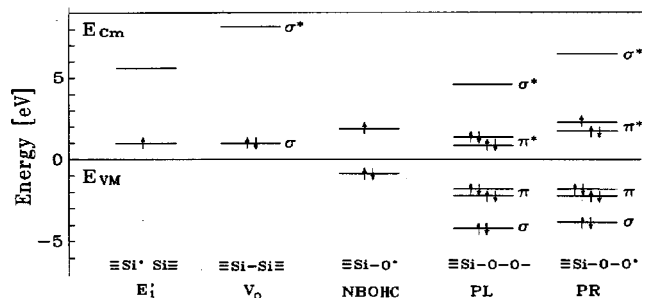

FIG. 6. The energy levels of the defect centers in a-SiO_2.

Downloaded 22 Dec 2004 to 139.174.155.153. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

charging can be expected if the captured electrons are related to them. The annealing behavior of the radiation-induced defects, such as E' center, NBOHC, and PR, has been studied with ESR in combination with optic spectroscopy by Stapelbroek *et al.*[29] The concentrations of E' center and ''wet'' NBOHC (from OH group) drop markedly with increasing annealing temperature. At a temperature of 300 °C 90% of the E' center and 80% of the NBOHCs could be annealed. In contrast, between 300 and 400 °C, the PR reaches its maximal concentration. It is completely annihilated for annealing temperature higher than 600 °C.

The charges in our a-SiO_2 sample sustain up to the annealing temperature higher than 650 °C, and this agrees well with the results reported by Aitken, Young, and Pan[2] and Stapelbroek.[29] The remaining charge at this temperature can be attributed to the PRs in the sample, which can be initially induced by the irradiation or be the outcome from the annealing of E' center and NBOHCs.[29,30] The higher annealing temperature can be understood from the fact that the rehabilitation of the regular bonds from a PR precursor is conditioned by the release of an oxygen atom.

V. CONCLUSIONS

Electron bombardment of SiO_2 produces not only an oxygen deficient surface due to ESD, but also damage deep inside the substance is introduced by radiolytic processes. The oxygen deficiency after a lasting radiation stretches into bulk by up to 25 nm, however, the defects from the radiolysis have a distribution along the trajectories of the primary electron, which corresponds to the energy dissipation of the primary electrons. The charging due to oxygen depletion at the surface can be compensated efficiently by environmental AES with O_2. This is achieved by compensation of the oxygen deficiency. As a result, the related trap centers are eliminated. E' center, NBOHC, and PR produced in the following radiolysis, can trap electrons and become charged-up negatively. Charges related to the bulk defects cannot be compensated with an O_2 environment. Each defect type has its own annealing temperature, so according to which defect is dominant in the irradiated sample (which depends again on the preparation condition of the sample and the irradiation parameters), the charging in AES behaves differently. Annealing of the defects leads to partial discharging, however, a complete charge compensation, for example, at 3 keV energy and 30° incidence can be expected by heating the sample support above 700 °C in the O_2 environment of 5×10^{-8} Torr O_2.

ACKNOWLEDGMENTS

The financial support of the Deutsch Forschungsgemeinschaft (SFB 180) is gratefully acknowledged. The authors thank Prof. G. Borchardt (Technisches Universität Clausthal) for providing us with some of the studied samples.

[1] J. P. Vigourous, J. P. Duraud, A. Le Moel, C. Le Gressus, and D. L. Griscom, J. Appl. Phys. **57**, 5139 (1985).
[2] J. M. Aitken, D. R. Young, and K. Pan, J. Appl. Phys. **49**, 3386 (1978).
[3] C. Le Gressus, D. Massignon, and R. Sopizet, Surf. Sci. **68**, 338 (1977).
[4] Y. E. Strausser and J. S. Johannessen, *Surface Analysis for Silicon Devices* (NBS Special Publ. 400–423), p. 125.
[5] H. Imai, K. Arai, J. Isoya, H. Hosona, Y. Abe, and H. Imagawa, Phys. Rev. B **48**, 3116 (1993).
[6] D. L. Griscom, *The Physics and Technology of Amorphous SiO_2* (Plenum, New York, 1988), p. 125.
[7] D. L. Carroll, D. L. Doering, and P. Xing-Skiba, J. Vac. Sci. Technol. A **41**, 2312 (1993).
[8] H. Guo, W. Maus-Friedrichs, and V. Kempter, Surf. Interface Anal. **25**, 390 (1997).
[9] G. Ohlendorf, W. Koch, V. Kempter, and G. Borchardt, Surf. Interface Anal. **17**, 947 (1991).
[10] J. S. Johennessen, W. E. Spicer, and Y. E. Strausser, J. Appl. Phys. **47**, 3028 (1976).
[11] L. Calliari, Nucl. Instrum. Methods Phys. Res. B **58**, 199 (1991).
[12] D.J.DiMaria, *The Physics of SiO_2 and its Interface* (Pergamon, New York, 1978), p. 160.
[13] D. R. Young, D. J. DiMaria, W. R. Hunter, and C. M. Serrano, IBM J. Res. Dev. **22**, 285 (1978).
[14] E. H. Nicollian, C. N. Berglund, P. F. Schmidt, and J. M. Andrews, J. Appl. Phys. **42**, 5654 (1971).
[15] H. Nishikawa, R. Nakamura, R. Tohmon, and Y. Ohki, Phys. Rev. B **41**, 7828 (1990).
[16] H. Guo, Ph.D. thesis, TU Clausthal, 1996, pp. 12, 67.
[17] E. P. O'Reilly and J. Robertson, Phys. Rev. B **27**, 3780 (1983).
[18] J. Robertson, *The Physics and Technology of Amorphous SiO_2* (Plenum, New York, 1988), p. 91.
[19] D. L. Griscom, Proceedings of the Annual Frequency Control Symposium, 1979, p. 98.
[20] M. E. Zvanut, F. J. Feigel, W. B. Fowler, and J. K. Rudra, *The Physics and Technology of Amorphous SiO_2* (Plenum, New York, 1988), p. 187.
[21] W. L. Warren, E. H. Poindextex, M. Offenberg, and W. Mueller-Warmuth, J. Electrochem. Soc. **139**, 872 (1992).
[22] N. Itoh, K. Tanimura, and C. Itoh, *The Physics and Technology of Amorphous SiO_2* (Plenum, New York, 1988), p. 135.
[23] A. Edwards and W. Fowler, Phys. Rev. B **26**, 6649 (1982).
[24] S. T. Pantelides and W. A. Harrison, Phys. Rev. B **13**, 2667 (1976).
[25] K. L. Yin and W. B. Fowler, Phys. Rev. B **10**, 1391 (1974).
[26] H. Nakatsuji and H. Nakai, Chem. Phys. Lett. **174**, 283 (1990).
[27] H. Holleck, *Hartstoffschichten zur Verschleissminderung* (DGM, Oberursel, 1987), p. 25.
[28] Y. Cross and J. C. Rostaing, *The Physics and Technology of Amorphous SiO_2* (Plenum, New York, 1988) p. 337.
[29] M. Stapelbroek, D. L. Griscom, E. J. Friebele, and G. H. Siegel, J. Non-Cryst. Solids **32**, 313 (1979).
[30] R. L. Pfeffer, *The Physics and Technology of Amorphous SiO_2* (Plenum, New York, 1988), p. 181.

Downloaded 22 Dec 2004 to 139.174.155.153. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp