IMPROVEMENT IN RADIATION HARDNESS OF OXIDE BY SUCCESSIVE IRRADIATION-THEN-ANNEAL TREATMENTS

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Abstract—It was experimentally observed that MOS devices prepared by repeated irradiation-then-anneal treatments were more radiation hard than those without such treatments. A modified isochronal annealing method based on the newly reported flat-band-condition annealing approximation was used in this work to examine the activation energy distribution of the radiation-induced positive charges. It was found that an MOS device after X-ray irradiation with a dose rate of 200 k rads (SiO_2)/min for 5 min exhibited a distribution of activation energy ranging from 1.2 to 1.8 eV. A sample which was subjected to a repeated irradiation-then-anneal treatments exhibited a significant reduction in the distribution of activation energy in the low energy region of 1.2–1.5 eV, but not in the high energy region of 1.5–1.8 eV. The activation energy distribution for samples prepared under various postoxidation treatments are discussed.

1. INTRODUCTION

A radiation-hard oxide is important for an integrated-circuit (IC) to achieve long-term stability. Several methods are proposed to make the oxides more radiation-hard[1–3]. These workers employed fabrication variations, e.g. process optimization[1] or double layer structure[3], to attain their goals. It is essential that the fabrication procedures used to obtain the radiation-hard oxides should be compatible with the existing IC processes.

In this work, we propose a simple way to efficiently reduce the radiation sensitivity of oxide which requires no fabrication variations. It is well known that the number of radiation-induced positive charges near the SiO_2/Si interface is strongly dependent on the interfacial strain[4–6]. The larger the interfacial strain, the worse the radiation hardness of oxide. It can be explained by a model in which the ionizing radiation breaks a strained bond leaving an Si^+ site, which is the trapped hole, and a mobile nonbridging oxygen that propagates, by the action of the strain gradient, toward the interface[4]. Therefore, we believe that radiation releases the interfacial strain although it introduces positive charges near the SiO_2/Si interface. Fortunately, most of the radiation-induced positive charges can be annealed out at a suitable temperature or ambient[7,8]. So, if a sample is first irradiated and then annealed, it will become more radiation hard than that without such treatment since its interfacial strain has been suitably released. This phenomenon was experimentally observed in this work based on the $C-V$ measurements. The irradiation-then-anneal procedure can be repeatedly carried out until the sample reaches a certain saturated radiation hardness level, beyond which there is no significant improvement.

In addition to the $C-V$ measurements, the activation energy distributions for the samples with and without successive irradiation-then-anneal treatments were also examined. There are several ways to obtain the activation energy distributions of the radiation induced damage[7,9–11]. We realized that the residual charges left behind the metal gate (or the substrate) of an MOS device after $C-V$ measurement might affect the anneal behavior significantly. A technique called flat-band-condition annealing approximation was proposed to exclude the field-assisted effect during annealing[12]. In this work, a modified isochronal annealing method was developed based on the above technique. The activation-energy distribution of an X-ray irradiated sample was found to be in the range of 1.2–1.8 eV. It was observed that the change of effective charge number density in the low activation energy range of 1.2–1.5 eV was reduced by successive irradiation-then-anneal treatments or by postoxidation cooling in an ambient containing oxygen, but no such reduction in the change of effective charge number density was seen in the high activation energy range of 1.5–1.8 eV. We give some possible explanations for this phenomenon based on the strain-related mechanism.

2. EXPERIMENTAL

p -Type and n -type silicon wafers with (100)-orientation were used as the substrates of the MOS devices. After standard cleaning procedures, these wafers were dry oxidized at 900°C in a (3%) HCl ambient. After oxidization, most of the samples were first postoxidation annealed (P.O.A.) and then cooled in an N_2 ambient. It is known that samples prepared under various oxidation conditions will exhibit

different sensitivities to irradiation[1]. In order to compare the radiation hardness between the sample prepared by successive irradiation-then-anneal treatments and that by a radiation-hard oxidation process, some samples after oxidization were cooled in an $N_2 + O_2$ ambient without P.O.A. treatment. The final oxide thickness of these samples was about 350 Å. Aluminum was used as the material for the gate and the backside contacts. Finally, the MOS devices were postmetallization annealed at 400°C in an N_2 ambient for about 30 min.

An MOS(*p*) device (P.O.A. and cooled in N_2), i.e. sample A, was successively irradiated and then annealed. A dose rate of 200 k rads(SiO_2)/min and an irradiation time of 5 min were used for X-ray irradiation. An anneal temperature of 400°C and an anneal time of 30 min were employed. After first anneal, the capacitance values were measured when the gate voltage was varied from -4 to +2 V and then from +2 to -4 V. Such a characteristic is shown as curve no. 1 in Fig. 1(a). The device was subjected to irradiation and the above *C-V* measurement was repeated. The *C-V* characteristics are shown by two curves marked "1" and the two curves are due to the hysteresis loop. The hysteresis is due to increased slow trap states. The successive annealing resulted in curve 2 and the subsequent irradiation resulted in curves 2'. The *C-V* characteristics after the fourth annealing and irradiation are shown by curves 3 and 3' respectively.

The flat-band voltage V_{FB} obtained from the *C-V* characteristics are shown in Fig. 1(b). The plot of V_{FB} as a function of number of anneal/irradiation treatments is shown in the figure. There are two values of V_{FB} for an irradiation due to the hysteresis loop. The value of V_{FB} remained practically constant after each annealing treatment. That is to say, the radiation-

induced damage can be removed by annealing. Interestingly, the radiation sensitivity of this device decreases, i.e. the value of V_{FB} after X-ray irradiation and subsequent anneal becomes small, as the number of successive irradiation-then-anneal treatment increases. After about four such treatments, the radiation sensitivity becomes almost saturated. Under such circumstances, the flat-band voltage shift ΔV_{FB} after X-ray irradiation is reduced to about the half of that without treatment. The radiation hardness of the oxide had finally been significantly improved.

Similarly, an MOS(*n*) device (P.O.A. and cooled in N_2), i.e. sample B, with an oxide thickness of 350 Å was also examined. Figure 2(a) shows some of the obtained *C-V* curves. It is noted that the radiation behavior of an MOS(*n*) device is generally different from that of an MOS(*p*) device[13,14]. Briefly, the variation of the V_{FB} for an MOS(*n*) device after irradiation is much smaller than that for an MOS(*p*) device. The effects of work function difference[13] and interface states[14] mainly account for this phenomenon. In order to describe the radiation hardness property clearly, only two sets of *C-V* curves are presented in this figure. Curve no. 1 is the *C-V* curve after the first annealing. After the first irradiation, the *C-V* curve is seriously distorted, as shown by curve no. 1'. The irradiation-then-anneal treatment was repeatedly carried out as described above. Curve no. 2 is the *C-V* curve after the seventh annealing, which coincides with curve no. 1. After the seventh irradiation, the *C-V* curve is still distorted, as shown by curve no. 2'. However, it is obvious that this curve is steeper than curve no. 1'. This is due to the fact that the number of interface states for curve no. 2' is much smaller than that for curve no. 1'. Also, when we compare the mid-gap shifts for these curves, we see that the number of the net fixed charges for

Fig. 1. (a) The *C-V* curves of an MOS(*p*) device after the first, the second, and the fourth annealings and irradiations. (b) The flat-band voltage V_{FB} vs the number of treatment for this device after each annealing or irradiation.

Fig. 2. (a) The C - V curves of an MOS(n) device after the first and the seventh annealings and irradiations. (b) The flat-band voltage V_{FB} vs the number of treatment for this device after each annealing or irradiation.

curve no. 2' is smaller than that for curve no. 1'. Figure 2(b) shows V_{FB} vs the number of treatment of this device after each annealing or irradiation. It is also clear from these figures that the radiation hardness of the oxide had been improved by the successive irradiation-then-anneal treatments.

In order to show the importance of carrying out the irradiation steps in the hardening procedure, i.e. the successive irradiation-then-anneal treatments, some other samples (P.O.A. and cooled in N_2) were examined as follows. Four MOS(p) and four MOS(n) devices with oxide thickness of 350 Å were postmetallization annealed in an N_2 ambient for 0.5, 1, 2 and 3 h, respectively. Then, they were X-ray irradiated with the same condition as those mentioned in Figs 1 and 2. Figures 3(a) and (b) show V_{FB} vs postmetallization anneal time for the MOS(p) and the MOS(n) devices, respectively, before and after irradiations. No improvement of radiation hardness is observed when postmetallization anneal time is increased. The

irradiation-then-anneal procedure improves the radiation. The radiation hardness is not achievable by merely increasing the anneal time without the irradiation step in between. Therefore the theory that the radiation releases the interfacial strain, and the subsequent annealing removes the positive charges introduced during irradiation, seems valid. For the samples prepared by a radiation-hard oxidation process, the irradiation experiments were also carried out. In Fig. 4, two MOS(n) devices, i.e. samples C and D, and two MOS(p) devices, i.e. samples E and F, are compared. Samples C and E were prepared by a regular process (P.O.A. and cooled in N_2), while samples D and F by a radiation-hard oxidation process (no P.O.A., cooled in $N_2 + O_2$). Figure 4(a) shows the C - V curves of samples C and D before and after X-ray irradiations. Curves no. 1 and 1' are the C - V curves of sample C before and after irradiation, respectively, while curves no. 2 and 2' are the C - V curves of sample D before and after irradiation,

Fig. 3. The flat-band voltage V_{FB} vs the postmetallization anneal time for (a) an MOS(p) and (b) MOS(n) devices before and after irradiations.

respectively. As can be seen from this figure, before irradiation, sample D (i.e. curve no. 2) contains more positive fixed charges than sample C (i.e. curve no. 1). This phenomenon probably accounts for the excess oxygen left at the SiO_2/Si interfacial region during the cooling procedure in an ambient containing oxygen. However, after irradiation, sample D (i.e. curve no. 2') is less sensitive to irradiation than sample C (i.e. curve no. 1'). Similarly, MOS(*p*) devices also appear to have the same radiation hardness as observed above. In Fig. 4(b), curves no. 3 and 3' are the $C-V$ curves of sample E before and after irradiation, respectively, while curves no. 4 and 4' are the $C-V$ curves of sample F before and after irradiation, respectively. Before irradiation, curve no. 4 contains more positive fixed charges than curve no. 3. After irradiation, curve no. 4' is less sensitive to irradiation than curve no. 3'. It is believed that the excess oxygen releases some of the interfacial strain and therefore hardens the oxide[15]. However, the release of interfacial strain due to excess oxygen is not so efficient as that by successive irradiation-then-anneal treatments. They will be compared in a later section.

3. ANALYSIS OF ACTIVATION ENERGY DISTRIBUTION

The change of effective charge number density as a function of activation energy is one of the important characteristics in examining the differences of the radiation effects between two different samples[9-11]. It is believed that the $C-V$ technique was usually used for the analysis. However, the final voltage of each $C-V$ measurement should be carefully considered since the residual charges left behind the metal gate (or the substrate) of an MOS device can exist for a long time even when the bias source is removed from the sample, and will cause varied annealing behavior due to the differences in the electric field (E_i) at the SiO_2/Si interface during annealing[12]. Because the characteristics of the existing residual charges at a particular annealing temperature is important to the analysis of the modified isochronal annealing method proposed later in this work, a more detailed characterization of the behavior of the existing residual charges at various temperatures should be carried out.

An experimental setup used for studying the decay characteristics of an MOS device as a function of temperature is shown in Fig. 5(a). The sample under test was charged to -5 V just before the start of the experiment. The decay behavior of the floating gate voltage V_G was measured with a high input impedance electrometer (Keithley 602 C). Figure 5(b) shows the results of an MOS(*p*) device tested at 27, 200, 250, 300, 325, 350 and 375°C, respectively. The corresponding RC time constants, which were determined according to the V_G 's read at $t = 5$ min, are also shown in this figure. It is clear from this figure that the decay of V_G at $t = 2$ min, which was chosen

Fig. 4. (a) The $C-V$ curves of two MOS(*n*) devices before and after irradiations. Sample C is prepared by a regular oxidation process (P.O.A. and cooled in N_2), while sample D by a radiation-hard oxidation process (no P.O.A. cooled in $\text{N}_2 + \text{O}_2$). (b) The $C-V$ curves of two MOS(*p*) devices before and after irradiations. Sample E is prepared by a regular oxidation process (P.O.A., and cooled in N_2), while sample F by a radiation-hard oxidation process (no P.O.A., cooled in $\text{N}_2 + \text{O}_2$).

Fig. 5. (a) An experimental setup used for studying the decay characteristics of an MOS device as a function of temperature. (b) The decay behavior of an MOS(*p*) device tested at 27, 200, 250, 300, 325, 350 and 375°C, respectively, from -5 V.

as the anneal time in each isochronal anneal as discussed later, is very small below 350°C.

For an MOS device with a flat-band voltage of V_{FB} , the relationship between the gate voltage V_G and the E_i can be expressed as:

$$V_G = V_{FB} + E_i d_{ox} + \psi_s, \quad (1)$$

where d_{ox} is the oxide thickness and ψ_s is the semiconductor surface potential. In order to maintain identical conditions during the annealing procedure, it was decided to keep $E_i = 0$ V/cm. Then it was necessary to charge the device to V'_{FB} , and V'_{FB} was the flat-band voltage measured by a C - V measurement before each flat-band-condition anneal. It is noted that if an irradiated MOS device is tested for C - V characteristics with a constant sweep rate in both the forward and the backward directions, two V_{FB} 's (see Figs 1 and 2) are obtained due to the existence of slow trap states. In order to exclude the effect of slow trap states on V_{FB} , the d.c. bias was maintained at the flat-band condition for a sufficiently long time. By placing this charged device in an annealing furnace with a temperature below 350°C for about 2 min, the flat-band-condition annealing approximation is achieved. Figure 6 shows the change of effective charge number density ΔN_{eff} vs time for two Co-60 irradiated MOS(p) devices annealed at 200°C under the flat-band condition and the short-circuit condition, i.e. $V_G = 0$. The ΔN_{eff} was obtained from the flat-band voltage shift ΔV_{FB} (with respect to the initial V_{FB}) according to the following equation:

$$\Delta N_{eff} = \frac{C_{ox}}{q} \Delta V_{FB}, \quad (2)$$

Fig. 6. The change of effective charge number density ΔN_{eff} vs time for two Co-60 irradiated MOS(p) devices annealed at 200°C under the flat-band and the short-circuit conditions, respectively.

Fig. 7. The change of effective charge number density ΔN_{eff} vs time for two MOS(p) devices annealed under the flat-band conditions. The solid circles are the results of a sample first annealed at 200°C then subsequently at 300°C while the solid triangles are the results of another sample annealed at 300°C only.

where C_{ox} is the oxide capacitance. It is interesting to note that the ΔN_{eff} obtained under the flat-band condition varies slowly with time, while the ΔN_{eff} obtained under the short-circuit condition changes rapidly with time. The E_i is positive under the short-circuit condition. Thus the annealing behavior is affected due to the detrapping of the holes from SiO_2 into Si[16]. The E_i thus plays an important role in the annealing behavior.

Temperature is also an important factor in determining the annealing behavior. Figure 7 shows ΔN_{eff} vs time for two MOS(p) devices annealed under the flat-band conditions. The ones denoted by the solid circles were obtained from a sample annealed first at 200°C then subsequently at 300°C, while the ones denoted by the solid triangles were obtained from a second sample annealed at 300°C only. For the former ones annealed at 200°C, the ΔN_{eff} changes very slowly with time, as observed in Fig. 6. As the temperature is increased to 300°C the ΔN_{eff} decreases linearly with time in a log plot. The observation is the same for the second case where the sample was annealed at 300°C only. The slope for the first case is -0.39. While for the later one the slope is -0.35. It is noted that a linear relationship between ΔN_{eff} and time in log scale implies a power law dependence of ΔN_{eff} on time[17]. The slope mentioned above represents the exponent of time, which is unitless in such case. Although the two reaction model proposed by Reed and Plummer[17] can partially explain the linear slope. The explanation for the temperature dependence of the slope is still lacking. The temperature dependence of the annealing behavior of ΔN_{eff} is examined by another method, the activation energy distribution.

Generally, the activation energy E_a for an annealing process carried out at a temperature T for t s can be approximately expressed by [9,18,19]:

$$E_a \cong kT \ln(\nu_0 t), \quad (3)$$

where ν_0 is a frequency factor. It is noted that the dependence of E_a on ν_0 is very weak, so the specific value of ν_0 is not critical [11,19]. In this work $\nu_0 = 10^{12} \text{ s}^{-1}$ was used. The flat-band-condition approximation is valid below 350°C , and the annealing characteristic is constant below 200°C as observed in Figs 6 and 7, a modified isochronal annealing method is proposed as follows. The device was annealed at flat-band condition for 120 s at temperatures from 150°C to 350°C in 10°C increments. Then, the E_a for each annealing step was calculated using eqn (3) with $t = 120 \text{ s}$ and T as a parameter. It was found that the activation energies varied from 1.2 to 1.8 eV. Figure 8(a) shows the effective charge number density N_{eff} vs E_a for an X-ray irradiated MOS(p) device, i.e. sample E annealed under the flat-band condition. It is noted that the N_{eff} was obtained from the flat-band voltage shift with respect to the ideal V_{FB} ($V_{\text{FB}} = -0.88 \text{ V}$). The activation energy distribution can be calculated by taking the negative derivative of N_{eff} with respect to E_a , i.e. $-dN_{\text{eff}}/dE_a$, as shown in Fig. 8(b).

We compared the activation energy distributions of three MOS(p) devices, i.e. samples A, E and F, prepared in different ways. Sample A was prepared by successive irradiation-then-anneal treatments as described in Fig. 1, sample E by a regular oxidation process (P.O.A. and cooled in N_2), and sample F by a radiation-hard oxidation process (no P.O.A., cooled in $\text{N}_2 + \text{O}_2$) as described in Fig. 4. Their activation energy distributions are shown in Fig. 9. It was observed that all the activation energies were

Fig. 8. (a) The effective charge number density N_{eff} vs the activation energy E_a for an X-ray irradiated device annealed under the flat-band condition for 120 s at temperatures from 150°C to 350°C in 10°C increments. (b) The change of effective charge number density, $-dN_{\text{eff}}/dE_a$, vs the activation energy E_a of the device mentioned in (a).

ranged from 1.2 to 1.8 eV, and the distributions of $(-dN_{\text{eff}}/dE_a)$ in the high energy region of 1.5–1.8 eV for all samples are almost the same. However, near the low energy range of 1.2–1.5 eV, the distribution of $(-dN_{\text{eff}}/dE_a)$ for sample A is the smallest one among three, and that for sample F is smaller than that for

Fig. 9. $-dN_{\text{eff}}/dE_a$ vs the activation energy for three X-ray irradiated MOS(p) devices annealed under the flat-band conditions. Sample A was prepared by successive irradiation-then-anneal treatments, sample E by a regular oxidation process (P.O.A. and cooled in N_2) and sample F by a radiation-hard oxidation process (no P.O.A., cooled in $\text{N}_2 + \text{O}_2$).

sample E. Therefore, a "hardening" procedure can reduce the distribution of $(-dN_{\text{eff}}/dE_a)$ near the low energy region. Interestingly, the "hardening" procedure of successive irradiation-then-anneal treatments is more efficient in the reduction than that of changing oxidation condition only. This observation is different from the result obtained in the Shanfield work[20]. It is probably due to the fact that the effect of the hardening process used in this work, i.e. successive irradiation-then-anneal treatments, is basically different from the effect of that used in the Shanfield work, i.e. postoxidation annealing. From the behavior observed in Fig. 9, it is believed that the low activation energies are related to the strain-induced hole trap centers, which can be eliminated by releasing the strain near the SiO_2/Si interfacial region via the "hardening" procedure, while the high activation energies are related to the intrinsic hole trap centers and are not affected by the oxide treatment. This explains the saturation behavior of the radiation hardness level observed in Figs 1 and 2.

4. CONCLUSIONS

Successive irradiation-then-anneal treatments provide a possible way for one to improve the radiation hardness of oxide. The modified isochronal annealing method used in this work excludes the field-assisted effect on annealing. Based on this method, the activation energy for the irradiation-induced damage was found to be within the range of 1.2–1.8 eV. The change of effective charge number density in the low activation energy range of 1.2–1.5 eV was reduced by the radiation hardening procedures proposed in this work and it is possibly due to the reduction in the strain-induced hole trap centers. But in the high activation energy range of 1.5–1.8 eV, such a reduction was not observed and it is possibly due to intrinsic hole trap centers.

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