phys. stat. sol. (a) 76, 107 (1983)

Subject classification: 13.3 and 14.3.3; 11; 22.6

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Accumulation and Discharging of the Hole Charge in Oxide Layers of MIS Structures

By

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Charge accumulation of non-equilibrium holes induced by X-ray irradiation is studied in silicon oxide layers of MIS structures. Thermal silicon dioxides obtained by oxidation in dry oxygen using chlorine technique as well as an anodic silicon dioxide are used as gate dielectrics. In all cases accumulation of approximately the same number of positively charged centers occurred after an X-ray exposure. Activation energy of isothermal annealing process is estimated as (0.2 to 0.5) eV.

Исследовано накопление в окисных слоях МДП-структур на кремнии заряда неравновесных дырок, возникших под влиянием рентгеновского излучения. В качестве подзатворного диэлектрика использовалась термическая двуокись кремния, полученная окислением в сухом кислороде и с использованием хлорной технологии, а также методами анодного окисления. Во всех случаях после облучения в окислах наблюдалось накопление примерно одинакого количества положительно заряженных центров. Величина энергии активации при изотермическом отжиге составляла (0,2 до 0,5) eV.

1. Introduction

The use of X-ray lithography and electron beam covering deposition methods in planar technology of semiconductor device manufacturing promotes the interest in studying changes in the electro-physical properties of insulator and semiconductor–insulator interface in MIS structures due to X-ray irradiation. Space charge accumulation and annealing in the dielectric and in surface states at the semiconductor–dielectric interface are of particular interest.

Charge accumulation induced by X-ray irradiation in thermal SiO_2 formed by oxidation in dry oxygen has been discussed in [1 to 6]. The effect of ionizing radiation on an anodically grown silicon dioxide has not been considered. It has been shown [7] that a high concentration of electron traps is observed in anodic silicon oxides. It is also known [5] that MIS structures with an Al_2O_3 gate dielectric showing high density of electron and hole traps exhibit high stability against irradiation. One can expect that anodic SiO_2, by analogy with aluminium oxides, would be more stable to irradiation effects. At the same time, according to the model of radiation-induced surface state generation [8], the presence of a great number of hydroxyl groups in anodic oxides as compared with thermally grown oxides should cause an increasing surface state density at the semiconductor–dielectric interface. The use of the chlorine technique for the thermal oxidation of silicon also changes the electro-physical properties of a silicon dioxide [9]. Thus, it seems to be interesting to compare the accumulation and discharging of the radiation-induced charge in silicon oxides which have the same structure but were formed by different techniques.

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2. Experimental

The kinetics of radiation-induced charge accumulation and annealing in the oxide layer and in surface states at the silicon–silicon dioxide interface in MIS structures has been studied in this work. Silicon dioxides produced by thermal oxidation at 1000 °C in dry oxygen and at 1150 °C in dry oxygen with HCl admixture and by anodic (galvanostatic followed by potentiostatic) oxidation in 0.04 N solution of KNO_3 in ethylenglycole were used as gate dielectrics in a MIS structure with an area 5×10^{-3} cm^2. The gate dielectric thickness varied from 400 to 1200 Å. The irradiation was performed using an X-ray apparatus "Dron-2" with Cu anode; the mean energy of the non-monochromatized beam was equal to 10 keV. The absorbed dose was calculated according to [10] and was found to be 3.3×10^7 rd for $t = 1$ min at exposure to 1.25×10^8 R. The exposure dose was measured by a dosimeter "DRGZ-02".

The technique used in this study was a high-frequency capacitance–voltage (C–U) technique. Since the charge accumulated in the dielectric during X-ray exposure discharged significantly at room temperature, C–U characteristic measurements were performed 5 to 10 min after X-ray exposure.

3. Results and Discussion

The flat-band voltage of initial MIS structures was $U_{FB} = (1$ to $2)$ V, the density of surface states $N_{ss} = (1$ to $3) \times 10^{11}$ cm^{-2} eV^{-1}. The C–U chracteristics contained no hysteresis. After X-ray exposure the hysteresis was observed in the C–U curves for MIS structures with a "dry" thermal oxide and its magnitude increased with exposure dose approaching 1 V at an absorbed dose $D = 10^8$ rd. Simultaneously an increase of the surface state density N_{ss} was observed. In structures containing HCl oxides the quantity N_{ss} also increased to $N_{ss} = 10^{12}$ cm^{-2} eV^{-1}. In the case of MIS structures with anodic oxide the hysteresis did not appear on the C–U curves and the surface state density did not increase in these structures. The character of the dose dependence of the radiation-induced change of the flat-band voltage shift ΔU_{FB} was the same in structures with anodic and thermal oxides and corresponded to positive space charge accumulation in the dielectric.

Fig. 1 shows the X-ray dose dependence for the C–U characteristics of a MIS structure with anodic silicon oxide as an example. One can see that the C–U characteristics shift to the negative voltage region during X-ray exposure corresponding to positive charge accumulation in the dielectric. At the same time the slope of the C–U curves remains constant for MIS structures with anodic silicon oxide. In MIS structures with thermal and chlorine oxides the slope of the C–U characteristics increased due to the increase in surface state density at the interface.

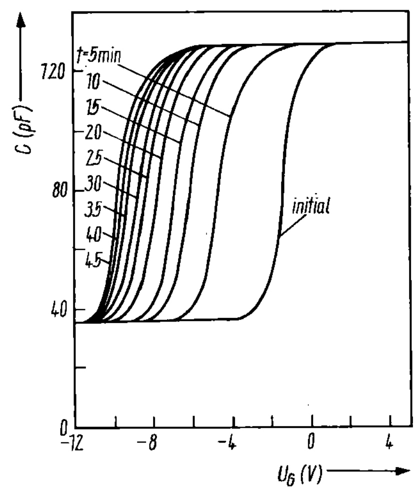

Fig. 1. C–U characteristic changes vs. X-ray exposure time t for a MIS structure with anodic oxide SiO_2 $d_{ox} = 1250$ Å

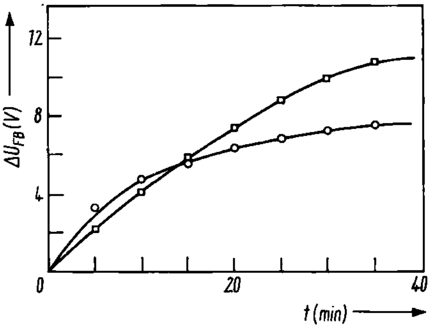

Fig. 2. Flat-band voltage change ΔU_{FB} as a function of the exposure time for a MIS structure. The exposure dose rate $N = 2 \times 10^6$ R/s. □ thermal oxide, $d_{ox} = 1000$ Å; ○ anodic oxide, $d_{ox} = 1000$ Å

Fig. 2 demonstrates the flat-band voltage change with irradiation time t for structures with anodic and thermal oxides. The maximum radiation-induced change ΔU_{FB} for structures with 1000 Å oxide was determined to be (8 to 10) V corresponding to positive charge accumulation both for anodic and thermal silicon oxides. It can be seen from Fig. 2 that saturation of the radiation-induced change of the flat-band voltage ΔU_{FB} occurs in $t \approx 30$ min which corresponds to an absorbed dose $D \approx 10^9$ rd. A similar dependence has been observed for all gate dielectric thicknesses. The maximum change of the flat-band voltage ΔU_{FB} depended on the gate dielectric thickness. This dependence is illustrated in Fig. 3. The absorbed dose was about 10^9 rd. It can be seen that the relation between ΔU_{FB} and the oxide thickness is described by a linear law $\Delta U_{FB} \sim d_{ox}$ for both types of oxides indicating accumulation of a constant in the oxide during X-ray exposure of structures with different oxide thicknesses.

Discharging of the accumulated charge in the dielectric and in surface states was observed at zero gate voltage in a temperature range $T = (100$ to 200 °C). The kinetics of the C–U characteristic changes at 100 °C is shown in Fig. 4 for MIS structures with thermal oxide. As the time of low-temperature annealing increases the decrease of the amount of charge in the oxide, the surface state density, and the hysteresis magnitude on C–U curves is apparent. Annealing at $T = 200$ °C for 30 min results in returning of the C–U characteristics of the MIS structure to the original state.

Isothermal annealing curves of the flat-band voltage change ΔU_{FB}, as a function of time t at constant temperature are plotted in Fig. 5. Discharging of the trapped charge causes changes in flat-band voltage ΔU_{FB} with time t following the power law $\Delta U_{FB} \sim t^n$, where "n" increases with the growth of d_{ox} and varies from 0.2 for the anodic oxide at $T = 100$ °C to 1.5 for the thermal oxide at $T = 100$ °C. It follows from Fig. 5 that the discharging of the accumulated charge is slower in the anodic oxide than in the thermal one. The radiation-induced charge discharging in MIS

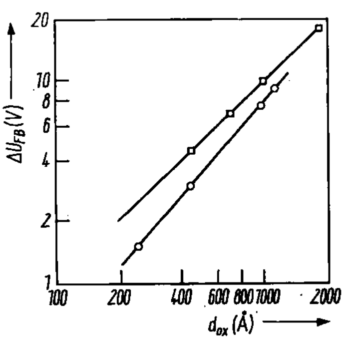

Fig. 3. The dependence of the radiation-induced flat-band voltage change ΔU_{FB} on the oxide thickness d_{ox}. The absorbed dose was about 10^9 rd. □ thermal oxide; ○ anodic oxide

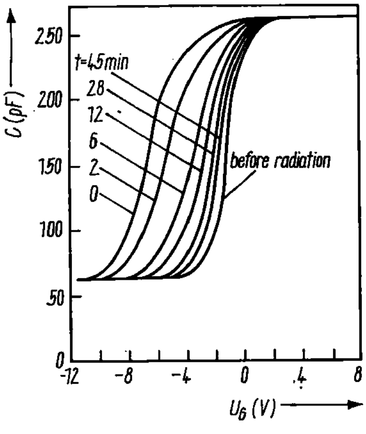

Fig. 4

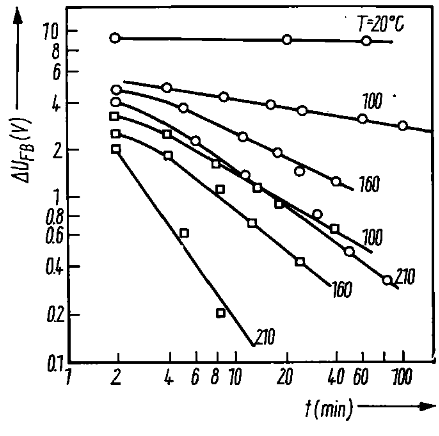

Fig. 5

Fig. 4. C–U characteristic change during isothermal annealing of the MIS structures with a thermal oxide SiO_2, $d_{ox} = 600$ Å, $T = 100$ °C

Fig. 5. Flat-band voltage change dependence on isothermal annealing time for MIS structures with the oxide thickness $d_{ox} = 1000$ Å at various temperatures. ○ anodic oxide; □ thermal oxide

structures with the chlorine oxide was still slower. The calculations of activation energy for the isothermal annealing process according to [11] indicated that the activation energy $E_a = (0.4$ to $0.5)$ eV for anodic and HCl oxides and $E_a = (0.2$ to $0.15)$ eV for SiO_2 thermally grown in dry oxygen. As a result of such a difference between the activation energies the isothermal annealing curve at $T = 210$ °C for MIS structures with the anodic oxide practically coincided with that for MIS structures with thermal oxide at $T = 100$ °C. The effective amount of the trapped positive charge in the dielectric calculated from the maximum change of the flat-band voltage $\Delta U_{FB} \approx 10$ V was estimated as $\Delta N_{ox} \approx 2 \times 10^{12}$ cm^{-2} for MIS structures with the anodic oxide and dry and "chlorine" thermal oxides.

It should be noted that electron traps which were observed in anodic silicon oxides [7] exhibited no radiation-induced charge in both accumulation and discharging kinetics. It is typical that on exposure to ionizing radiation the anodic oxides SiO_2 did not show an increase of the surface state density N_{ss}. This is in contrast with the models [5, 8] where such an increase did take place and was explained due to the pressure of hydroxyl groups.

4. Conclusions

Studies of radiation-induced charge accumulation in the dielectric of MIS structures showed that positive charge is accumulated in thermal (dry and chlorine) and anodic silicon oxides. Radiation-induced charge anneals well at elevated temperatures. The activation energy is of the order (0.2 to 0.5) eV.

Acknowledgements

The authors express their thanks to E. G. Kucherova and A. F. Akulov for valuable assistance in performing this work.

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(Received November 15, 1982)