ESP PHOTOMEMORY CENTERS IN THE $Si-SiO_2$ STRUCTURE

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It is known that defects in semiconductor-dielectric structures can be responsible for long-term optical memory. Information on the nature of these centers can sometimes be obtained by the ESP method [1]. The present paper is concerned with an investigation of the $Si-SiO_2$ structure subjected to UV radiation.

The ESP spectra were recorded on an EPR-3 spectrometer with operating frequency of 10 GHz and sensitivity of not less than 10^{11} spin/gauss. The studies were performed with Si (n type, ρ = 1000 ohm•cm) monocrystals, vibration-pulverized under vacuum. The specimens were then oxidized in oxygen at T = 1000-1100°C for 4 hr. Then the specimens were illuminated by a DKSSh-100 xenon lamp upon continuous rotation of a quartz ampule with a specimen. All the experiments were performed under a vacuum not poorer than 10^{-6} mm Hg.

It was found that oxidation of Si results in the appearance of two ESP signals, I_1 and I_2 (Fig. 1), the parameters of which are close to the parameters of signal detected by Kropman, et al. [2]. Signals I_1 and I_2 were easily saturated at microwave powers of ~1 mW. Vacuum heating did not change the intensity of signal I_1, while increasing somewhat the intensity of signal I_2 (Fig. 2a). Ultraviolet irradiation of the starting oxidized Si did not modify signals I_1 and I_2, nor did it cause the generation of new signals. Unlike this, UF irradiation of specimens heated under vacuum was accompanied by a significant rise in signal I_2, with the intensity as a function of the vacuuming temperature (Fig. 2b) (the intensity of signal I_1 did not change after UV irradiation). As is seen from Fig. 2c, vacuum heating of a preirradiated specimen reduces the level of signal I_2. Multiple alternation of vacuum heating UV irradiation resulted in reversible changes of signal I_2.

The parameters of signals I_1 and I_2 (the g factor, line width and the UHF power at which saturation occurs) are in satisfactory agreement with the corresponding characteristics of signals from E_1' and E_2' centers in quartz and germanium glasses subjected to high-energy irradiation [3, 4]. It can be presently regarded as established that oxygen vacancies are responsible for the E_1' signal [5], whereas the E_2' signal is preferably associated with the oxygen vacancy + oxygen complex in the interstice.

The region of localization of paramagnetic centers was determined by HF etching of previously irradiated specimens. It was found that intensity I_2 decreases 5-6 fold, whereas I_1 does not change much. Etching in a type CP agent

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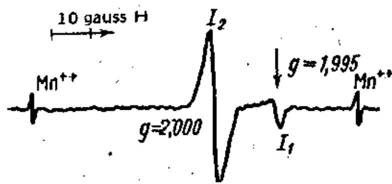


Fig. 1

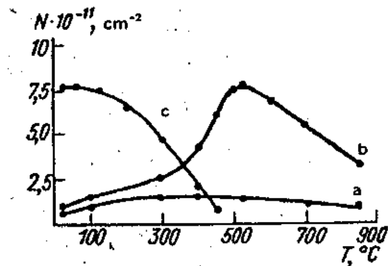


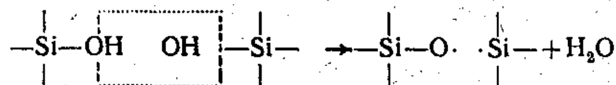
Fig. 2

Fig. 1. Typical ESP spectrum following the irradiation of an $Si-SiO_2$ structure.

Fig. 2. Concentration of paramagnetic centers I_2 vs vacuum-heating temperature: a) prior to UV irradiation; b) following UV irradiation; c) vacuum anneal of an UV irradiated specimen.

fully destroyed both signals. The qualitative conclusions that can be drawn from this are as follows. A significant part of centers I_1 is localized in the oxide layer (centers I_2^0); this group of centers vanishes when SiO_2 is dissolved in HF. Virtually all the I_1 centers and a small part of I_2(centers I_2^{intf}) are situated in the immediate proximity of the $Si-SiO_2$ interface; this group of centers vanishes only after etching the silicon. The existence of oxygen vacancies (I_1 centers) and vacancy + oxygen complexes (I_2^{intf} centers) in the transition $Si-SiO_2$ layer is in satisfactory agreement with a large volume of electron-microscopy data (among others the paper by Ishizaka, et al. [6]), according to whom the layer consists of SiO_x groups, where $x < 2$. Ultraviolet irradiation does not modify I_1 or I_2^{intf}. Apparently the energy location of these centers is such that in their initial state they are positively charged and paramagnetic.

The behavior of centers I_2^0 is different. Ultraviolet irradiation of vacuum-heated specimens results in a significant rise in I_2. Apparently, this is due to the fact that I_2^0 centers localized in the oxide have an energy location different than these very centers localized near the interface (I_2^{intf}). Prior to irradiation the I_2^0 centers are neutral and nonparamagnetic. Injection of holes, generated by UV irradiation from Si to SiO_2 [7] moves these centers to a positively charged paramagnetic state. The fact that irradiation results only in recharging of existing states, and not generation of new defects (or photochemical reaction), points to reversibility of the variation in I_2^0 with respect to anneal-reirradiation cycels. As is seen from Fig. 2b, photoactive I_2^0 centers arise in the oxide only after heating under vacuum. This may be associated with dehydration of $Si-SiO_2$, for example, according to the scheme:



$$-\mathrm{Si}-\mathrm{OH}\quad \mathrm{OH}-\mathrm{Si}- \rightarrow -\mathrm{Si}-\mathrm{O}\cdot\ \cdot\mathrm{Si}- + H_2O$$

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