

Dose dependent shift of the TL glow peak in a silicon rich oxide (SRO) film

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Thermoluminescence (TL) properties of UV irradiated silicon oxide films with silicon nano particles were investigated. The TL glow curve exhibits two symmetric glow peaks, one centered at about 120°C and the other one centered at around 240°C. The position of the peak maximum of the 120°C TL peak appears to shift to higher temperatures with increasing radiation dose while the high temperature peak shifts to lower temperature. The shift to lower temperature with increasing radiation dose of the 240°C peak is typical for a second order kinetics glow peak. The shift of the 120°C peak to higher temperature however is peculiar and is explained in this work as an effect of the multiple phase (silicon nano particles embedded in silicon oxide) nature of the film.

Keywords: Thermoluminescence; silicon; SRO; LPCVD.

En este trabajo se investigaron las propiedades de Termoluminiscencia (TL) de películas de óxido de silicio con exceso de silicio irradiadas con UV. La curva de emisión termoluminiscente exhibe dos picos simétricos, uno centrado en 120°C y la otra centrada en alrededor de 240°C. La posición del máximo pico de TL en 120°C parece correrse hacia altas temperaturas con el incremento en la dosis de radiación, mientras el pico que se encuentra a altas temperaturas se desplaza hacia temperaturas bajas. El corrimiento hacia temperaturas bajas con el incremento de la dosis de radiación del pico en 240°C es típico para un pico emisión cinético de segundo orden. El corrimiento del pico de emisión en 120°C hacia temperaturas altas sin embargo es peculiar y en este trabajo se explica como un efecto de la naturaleza multifases (nanopartículas de Silicio embebidas en el óxido de silicio) de la película.

Descriptores: Termoluminiscencia; silicio; SRO; LPCVD.

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1. Introduction

Optical and electrical properties of silicon-rich silica have been extensively investigated during the last decades due to the potential use of these materials in optoelectronic devices [1,2]. Many techniques have been reported to obtain SRO, including: co sputtering [3,4], RF glow discharge of SiH₄-O [5,6], Oxidation, ion-beam-assisted electron beam deposition [7,8], and CVD (Chemical Vapor Deposition) and combinations of these techniques with Si implantation [9-10]. Depending on the fabrication method and conditions SRO presents strong visible photo luminescence emission [11]. Emissions have been reported around 350 nm, 410 nm, 560 nm and 750 nm. The 350, 410 and 560 nm emissions have been ascribed to Si-O related species and oxygen vacancy related defects while the 750 nm emission is associated with some form of quantum confinement effect of the silicon clusters [12]. Evidence for the association of the 750 nm luminescence is the red shift and the decrease of intensity of this luminescence with increasing size of the silicon clusters [13-15]. In this study we investigated the UV induced thermoluminescence (TL) behavior of an annealed SRO film that contained principally 750 nm emission peak, in its photoluminescence spectrum and some emission

in the 300-475 nm range. The low temperature (120°C) TL peak shows a peculiar shift to higher temperature when the intensity of this peak increases. It is shown that this behavior can be explained by the multiple phase (silicon nano particles embedded in silicon oxide) nature of the film.

2. Experimental details

The samples used in this study were cut from a 550 nm thick SRO film deposited on an N type Si wafer with a resistivity in the range of 3-5 Ωcm. The film was prepared by the LPCVD (Low Pressure Chemical Vapor Deposition) method in a hot wall reactor at 700°C, using a mixture of N₂O and SiH₄ reactor gases. The ratio of the flow rates of the reactor gases, R₀=N₂O/SiH₄ was 20 which resulted in a silicon excess of 8%. After the preparation the samples were submitted to a heat treatment at 1100°C in a N₂ atmosphere for densification. After this treatment the samples contain nano particles of Si. The TL measurements were performed in an automated TL/OSL reader, model TL/OSL System TL-DA-15, fabricated by RISO, National Laboratory, Denmark. The TL reader was adapted for the possibility to perform UV-Vis illuminations. The light source comprises a 450 W Xenon

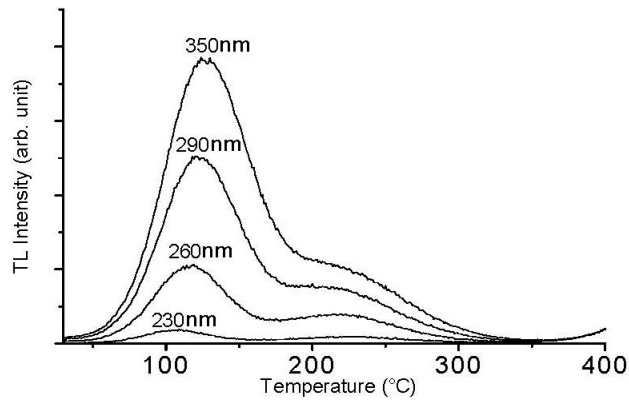


FIGURE 1. TL glow curves of the SRO film sample nr A42 after 300 s irradiation with 230, 260, 290 and 350 nm light and a 600 s storage.

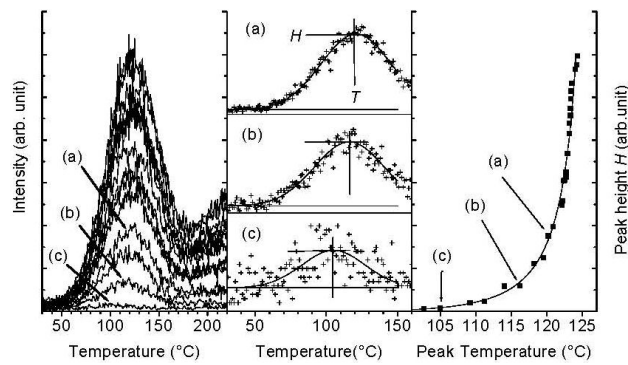


FIGURE 2. Raw data for the low temperature glow peak of sample B with different intensities (left graph). Gaussian shaped peaks were fitted to the data and from these fittings the peak positions T and intensities H were determined. In the middle graph are three examples a, b and c corresponding to the data a, b and c of the left graph. The determined intensities and positions (temperatures) are plotted in the right graph (scattered data points) together with a fitting of a proposed model for the shift (solid line).

lamp operated at 300 W, a home made shutter that could be gradually opened and a monochromator model GM252 (KRATOS). The intensity of the light at the sample position was about 3 mW/cm^2 for 300 nm and shutter completely opened. This was determined using a pyroelectric radiometer system model 7080 purchased from Oriel. A homemade computer program controlled the monochromator, the shutter and the TL/OSL system. All experiments in the TL-reader were performed in a N_2 environment.

3. Experimental results and analyses

To determine the TL glow curve, the sample was irradiated for 5 (sample A42) or 10 min (sample B) with UV light of wavelengths between 200 and 400 nm and additionally stored for 10 min to clean “fading sensitive glow peaks”. Figures 1 shows the results of the TL measurements for different irradiation wavelengths for the sample A42. It is seen that the shape of all glow curves is very similar except for a small

variation in the peak temperatures. These variations appear to be related to the intensity rather than the wavelength as was verified by TL measurements after irradiations with 350 nm light of different intensities (partially opened shutter). These measurements indicate that the first TL peak shifts to a higher temperature and the second peak to a lower temperature with increasing intensity.

The shift of the second peak of the TL glow curve to lower temperatures with increasing intensity (or dose) is typical for a non-first order glow peak. This effect has been well documented [16] and is related to the dependence of the recombination probability with the concentration of recombination centres. On the other hand the behaviour of the first TL glow peak, *ie* the shift to higher temperature with increasing intensity (or dose), has as far as we know never been described before. Here this behaviour is explained as a consequence of the presence of nano particles. The 120°C peak is treated as a distribution of first order peaks with their maxima at slightly different temperatures. The temperature at which the distribution has its maximum is considered as the average peak position of the individual peaks of the distribution weighted by their intensities. For the intensity of the peak, the peak height was taken. The position and peak height were determined by fitting a Gaussian function to the peak excluding the region where the peak overlaps with the second peak and taking into account the background signal. Figure 2 shows the procedure for sample B.

To explain the temperature shift of the peak we propose a model in which it is assumed that during the irradiation stage the radiation defects, say electrons and holes, are generated at the Si nano particles. Some of the electrons escape from the nano particles and get trapped at TL traps in the bulk material of the film preferentially close to the nano particle. The holes get trapped at not yet specified luminescence centers. Actually, for explaining the temperature shift of the TL peak, the details about how the holes reach the luminescence centers and the assignation of these centers is not important and here it is simply assumed that the hole is left behind at the nano particle. Further it is assumed that the TL peaks of the distribution corresponding to the electron traps closest to the

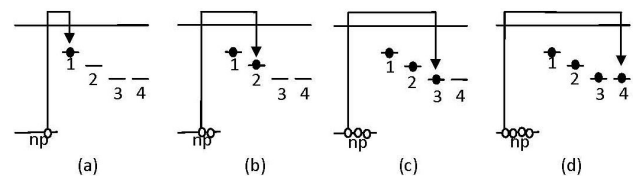


FIGURE 3. Energy level diagram of the model for the trap filing. At zero doses the defect \cdot , generated at the nano particle np by UV light, is trapped at trap 1, which is the trap closest to the nano particle np (a). As the dose increases, the subsequent generated defects at the nano particle are trapped at trap 2, 3 and 4 which are at increasing distance from the nano particle (b), (c), (d). The energy levels of the traps increase with the approximation of the trap to the nano particle due to crystal strain caused by the presence of the nano particle.

nano particle have the lowest peak temperature (or lowest activation energy). This may be thought of as an effect of crystal strain caused by the presence of the nano particle. Figure 4 shows an energy level diagram and the transfer processes during the irradiation stage corresponding to this model. The readout stage of the TL process is assumed to be similar to the usually assumed, *i.e.* during the heating the electrons are thermally released from the traps and transfer through the conduction band to the trapped holes where, upon recombination, a photon is emitted.

Within this model we make the following three assumptions:

(1) The dependence of the individual peak temperatures of traps on the distance (r) between nano particle and trap is:

$$T(r) = T_{\infty} - (T_{\infty} - T_0) \exp(-k_r r) \quad (1)$$

where k_r is the spatial alteration coefficient for the peak temperature, T_{∞} is the peak temperature of traps far away from the nano particle and T_0 is the peak temperature of traps closest to the nano particle

(2) Secondly we assume that the traps are distributed homogeneously over space. This implies that the number of available traps at a distant r from a nano particle increases proportional to r^2

(3) Finally we assume that the electrons generated during irradiation at a nano particle are trapped at nearest available traps. Thus when N electrons are generated at the nano particle, they are all trapped within a circumference R around the nano particle corresponding to a volume with N traps while all traps outside the circumference remain empty. Note that according to the first and second assumption, R is proportional to $\sqrt[3]{N}$. Since the intensity H is proportional to N , R is also proportional to $\sqrt[3]{H}$.

Using these three assumptions and additionally assuming that the nano particle is very small compared to the sphere of filled traps around the nano particle (so that we may integrate from the center of the nano particle) the average peak temperature can be expressed as:

$$T(H) = \frac{3}{H} \int_0^{\sqrt[3]{H}} (T_{\infty} - (T_{\infty} - T_0) \exp(-k_q q)) q^2 dq \quad (2)$$

with

$$k_q = k_r \cdot \left(\frac{4}{3} \pi V \rho_q \rho_T \gamma \right)^{-1/3}$$

and

$$q = r \cdot \left(\frac{4}{3} \pi V \rho_q \rho_T \gamma \right)^{1/3}$$

where ρ_q is the density of nano particles, ρ_T the density of traps, V is the volume of the sample and γ is a 'set up' parameter that relates the peak height with the number of filled traps. The solution for (2) is

$$T(H) = cT_0 + (1 - c)T_{\infty} \quad (3)$$

where c is:

$$c = \frac{6 - 3(Q^2 + 2Q + 2) \exp(-Q)}{Q^3}$$

$$Q = k_q \sqrt[3]{H}$$

The function $T(H)$ depends thus only on three parameters: T_{∞} , T_0 and k_q . Fitting this function to the scattered data points of the right graph of Fig. 3 leads to the solid line in this graph with parameter values $T_0 = 352$ K (79°C) and $T_{\infty} = 400$ K (127°C). The parameter k_q has the value 0.5185.

4. Conclusion

We have shown that the temperature shift as function of dose of the UV induced low temperature glow peak of SRO could be an effect of the confinement of the defect creation sites (at silicon nano particles). Good fitting results were obtained for a simple model based on the generation of radiation defects at the nano particles and subsequent trapping at traps in the bulk, in which it is assumed that (1) the traps are homogeneously distributed, (2) the traps closest to the nano particles are filled first and (3) the peak temperature of the traps obey: $T = T_{\infty} - (T_{\infty} - T_0) \exp(-k_r \cdot r)$ where r is the distance between traps and nano particles.

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