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Rate of F center formation in sapphire under low-energy low-fluence Ar^+ irradiation

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ABSTRACT

Ionoluminescence, optical absorption spectroscopy and Rutherford backscattering spectrometry channelling (RBS-C) have been used to study the rate of F center formation with fluence in 170 keV Ar^+ irradiated single crystals of α-Al_2O_3 (sapphire) at room temperature. Implantation fluences range between 10^{13} cm^{-2} and 5×10^{14} cm^{-2}. F center density (N_F) has been found to display an initial rapid linear increase with Ar^+ fluence followed by saturation to a maximum value of 1.74×10^{15} cm^{-2}. Experimental results show a 1–1 correlation between radiation damage in the oxygen sublattice and F center density. This suggest F center kinetics in sapphire under low-energy low-fluence Ar irradiation is a direct consequence of dynamic competition between oxygen defect creation and recombination. An attempt has also been made to extend this discussion to F center kinetics in sapphire under swift heavy ion irradiation.

1. Introduction

Unique thermal, optical, structural and chemical stability have made sapphire an attractive candidate for various technological applications [1,2]. Sapphire optical fibers, for example, have been considered promising candidates for in-pile instrumentation to predict behavior and performance in extremely high temperature radiation environments such as nuclear reactor cores [2]. In spite of its higher mechanical stability compared to quartz, continuous exposure of sapphire to radiations introduces point defects such as vacancies, interstitials and atomic impurities in its crystal lattice [3–5]. The resulting oxygen vacancies, V_O^{2+}, can trap one or two electrons forming F^+ and F centers respectively. These color centers modify the optical properties of sapphire. While F^+ centers are relatively easier to create, F centers are more stable at room temperature [6,1]. For better calibration and performance purposes of any sapphire optics related device, a clear understanding of F and F^+ center formation mechanism is therefore important.

Although considerable progress has been made over the past 60 years to understand radiation damage in sapphire, few fundamental issues remain unclear. Details of the electron capture process have not been clearly established. Equally, attempts to quantify V_O^{2+} in ion beam irradiated sapphire using optical spectroscopy have often resulted to significant disagreements between experimental and theoretical results [7].

In previous studies on swift heavy ions induced radiation damage in sapphire, Canut et al. [8] demonstrated that significant damage was caused by collective electronic excitation with the electronic damage cross section increasing linearly with electronic stopping power. They also obtained optical absorption bands at 4.8 eV, 5.4 eV and 6.1 eV typical to F and F^+ centers in sapphire. Recent works [9–11] show that the density of F centers (N_F) in swift heavy ion irradiated sapphire display a steep initial linear increase with irradiation fluence (ϕ) followed by a slow linear rise at higher fluences. This so-called two step F center kinetics was shown to demonstrated a clear correlation with sample swelling step height. It was hence attributed to damage induced structural changes such as ion track overlap near the bombarded sample surface.

In this work, we show that F center density in low-energy low-fluence Ar^+ irradiated sapphire displays an initial rapid linear increase with Ar^+ fluence and then saturate to a maximum value: irradiation conditions known never to produce swelling or overlapping ion tracks in sapphire [12–16]. We attribute this $N_F(\phi)$ behavior to a dynamic competition between defect creation and recombination. We also attempted an explanation to $N_F(\phi)$ kinetics in sapphire under swift heavy ion bombardment.

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2. Experiment

Double side EPI polished $10 \times 10 \times 0.43$ mm slices of Czochralski-grown (MTI Corporation, Richmond, CA) c-plane sapphire wafers with purity >9.99% and average roughness $R_a < 5$ Å were used in these experiments. To demonstrate that ion beam irradiation actually induces color centers in sapphire while simultaneously testing for the presence of any optically active impurities, a virgin sample was irradiated with 2 MeV He^+ ions for ionoluminescence (IL) studies. The resulting ion beam induced luminescence was fed into a multimode optical fiber placed 8 mm from the sample surface at an angle of 50°from the incident He^+ beam direction. This optical fiber then directed the light into an *ASEQ Instruments LR1- Compact Spectrometer* (Vancouver, Canada) fitted with a *Toshiba TCD1304DG* linear array having a spectral resolution <0.4 nm and a signal-to-noise ratio of 300:1. The resulting IL spectrum was then compared with known emission spectra of color centers in pure sapphire.

After confirmation of the sample purity, near surface point defects were created by irradiating seven samples with 170 keV Ar^+ corresponding to a projected range $r_p \approx 102$ nm, maximum electronic stopping power of 84 eV/Åand a maximum nuclear stopping power of 110 eV/Å according to the SRIM 2008 code [17]. The implantations were carried out at room temperature under a high vacuum atmosphere of 3×10^{-5} Torr. Implantation fluences ranged between 10^{13} and 5×10^{14} cm^{-2} at an average flux of 9.8×10^{12} $cm^{-2}\,s^{-1}$.

Optical absorption measurements were obtained at room temperature using a *Hitachi U-2001 UV/Vis Spectrophotometer* in the 190 nm to 1100 nm wavelength range. To ensure that the optical contribution of all radiation induced color centers is measured, light was passed through each sample in a direction parallel to the Ar^+ ion beam. Gaussian decomposition of peaks in the optical spectra was obtained using a data fitting program. F center density was determined using the Gaussian fit centered around 6 eV corresponding to F centers and the Smakula's formula [18]:

$$N_F = 2.01 \times 10^{17} \frac{n}{f(n^2+2)^2} OD_{max} W_{1/2}, \tag{1}$$

where $f = 0.92$ [19] is the oscillator strength of the optical transition, $n = 1.8$ the refractive index of sapphire corresponding to $h\nu \approx 6$ eV and $W_{1/2}$ the full width at half maximum of the peak with maximum optical density OD_{max}.

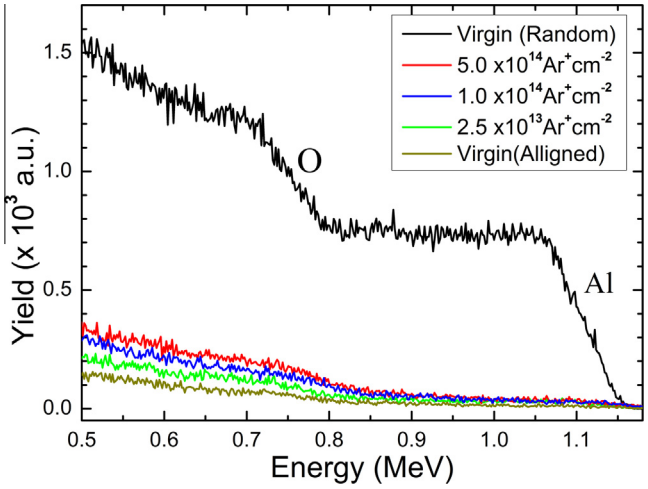

Fig. 1. RBS-C spectra of sapphire irradiated with 170 keV Ar^+. A 2.8% normalized minimum yield in the aligned virgin sample near the high energy surface of the Al sub-lattice implies a good crystalline sample. RBS-C shows some relatively small damage in the Ar implanted sample.

Radiation damage in sapphire was further analyzed using RBS-C generated with the help of a 15 keV resolution silicon barrier detector coupled to a 40 keV resolution multichannel analyser. A 2 MeV $^4He^+$ beam with current I = 15 nA, spot size diameter $d = 1$ mm generated by an RF source and accelerated through a 1.7 MV tandem accelerator was used. The target sample was mounted on a three-axes goniometer head with an average rotational resolution of 0.01°. To prevent accumulation of charge on each sample, 20–30 nm of gold film was deposited on their surface. Relative damage, F_d, induced by 170 keV Ar^+ was obtained using the classical formula [20]:

$$F_d = \frac{\chi - \chi_v}{1 - \chi_v}, \tag{2}$$

where χ is the normalized minimum yield of the Ar irradiated sample around r_p and χ_v the normalized minimum yield of the virgin sample.

3. Results, analysis and discussions

3.1. RBS-C analysis

Fig. 1 presents a comparison of the RBS-C spectra of virgin and 170 keV Ar^+ irradiated sapphire. A minimum yield of 2.8% near the high energy surface in the Al spectrum of the aligned virgin sample indicates a good quality crystal. Within the resolution limits of our experimental setup, there is no significant difference in the minimum yield of the Al sublatice of the samples for energies between 0.85 MeV and 1.15 MeV. This indicates that the 170 keV Ar beam does little damage to the Al sublattice; confirming the radiation hardness of sapphire [1]. However, there is a slight increase in the minimum yield of the implanted sample for energies less than 0.85 MeV. This energy range contains the spectra of both Al and O sublattices, making it impossible to extract radiation damage in the O sublattice alone. However, due to lack of significant damage in the prior Al sublattice, its logical to assume that changes in the minimum yield at this energy range are predominantly due to damages in the O sublattice. Using Eq. (2) for the O sublattice near r_p (*i.e.* $0.5 < E/\text{MeV} < 0.6$) we obtain a plot of radiation damage versus fluence, Fig. 2. Our experimental results fit well with a Poisson law similar to that previously used by Kabir et al. [9]:

$$F_d(\phi) = F_{sat}(1 - \exp(-\sigma\phi)), \tag{3}$$

where

$$\sigma = 2.26 \times 10^{-14}\ \text{cm}^2 \tag{4}$$

and

$$F_{sat} = 11.8\% \tag{5}$$

are respectively the damage cross section and partial disorder parameter at saturation.

According to the Kinchin–Pease model [14], low-energy low-fluence ion implantations in sapphire induces predominantly point defects. Also, recent experimental and theoretical results confirm the absence of defect microstructures such as voids, bubbles and ion tracks in sapphire under 170 keV Ar^+ irradiation at fluences between 10^{13} cm^{-2} and 5×10^{14} cm^{-2} [12,15]. Fig. 2 therefore suggest a dynamic competition between point defect build-up and recombination. As implantation fluence increases, defect build-up balances defect recombination leading to saturation. This increase in defect recombination with fluence can be due to increase in Frenkel pair (FP) mobility with sample temperature during implantation. The longer the implantation time (high fluence), the higher