Thermoluminescence of Al_2O_3 crystals grown by temperature gradient techniques

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Color center concentrations of the Al_2O_3 crystal grown by temperature gradient techniques were calculated from Gaussian fits to absorption spectra. The concentrations for F^- - and F^+ -centers at 204, 232, and 255 nm were determined to be 1.361×10^{17} , 0.098×10^{17} , and $0.325 \times 10^{17} \text{ cm}^{-3}$, respectively. Studies have shown that the thermoluminescence (TL) glow curve exhibits a prominent 450 K peak that matches well the first-order fitting curve. The thermal activation energy E and frequency factor s of the trap were determined to be $0.94456 \pm 0.00545 \text{ eV}$ and $5.8703 \times 10^{11} \text{ s}^{-1}$. With this theoretical analysis, a simple one-trap/one-center TL model is presented to provide a theoretical explanation of the TL process.

Al_2O_3 , color centers, thermoluminescence, absorption spectrum, TGT, crystals, curve fitting

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Over the past several decades, the color centers of Al_2O_3 single crystals have been studied through particle (electron, neutron, and ion) bombardment and ion-implantation [1–4]. Previous studies clearly indicate that at least two kinds of defect exist in Al_2O_3 . One is the F -type (F and F^+) center (an oxygen-ion vacancy occupied by two or one electron), the other is the V -type center (other ions adjacent to an aluminum vacancy). Color centers are strongly influenced by the growth procedure. Our previous studies [5] have shown that color centers of Al_2O_3 crystals grown under an oxidizing atmosphere are quite different from those grown under a reducing atmosphere. The F -type center is associated with atomic-displacement-type damage and its concentration is quite low in Al_2O_3 crystals grown under an oxidizing atmosphere before neutron irradiation. In contrast, Al_2O_3 crystals grown under a strongly reducing atmosphere show high concentration of F -type centers even without irradiation.

TL measurements are an effective way to identify color

centers in crystals after irradiation. Much work [6–9] has been done to study the TL properties of Al_2O_3 crystals in the range 90–500 K. These studies have shown that TL peaks at 60, 100, 220, 260, and 290 K were associated with F -type centers and 435 K peak was attributed to V -type centers. Little work has been done though on the TL properties of Al_2O_3 crystals grown in a reducing atmosphere.

In this paper we present calculations of the color-center concentrations of the Al_2O_3 crystals grown under a reducing atmosphere by temperature gradient techniques (TGTs). The TL glow curve, which was different from that of previous reports, was also analyzed by first-order kinetic curve fitting. Based on the fitted parameters, a simple model was developed to enable a theoretical analysis of experimental TL data.

1 Experiments

Al_2O_3 crystals were grown by the TGT; the details have been given previously [10]. High-purity Al_2O_3 crystals were

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weighed and pressed into cylindrical blocks with diameters close to the inner diameter of a Mo crucible. Before loading these blocks into the crucible, a cylindrical seed crystal with a (11 $\bar{2}$ 0) orientation was placed in the seed holder. The growth process requires the furnace to have a high vacuum (10^{-3} Pa), filled with high purity Ar gas, then heated to melt the materials in the crucible, which were then kept molten for 3 h. Growth was then initiated by slowly lowering the temperature at a rate of 2 K h $^{-1}$. The after-growth cool-down rate was also tailored to the crystal geometry. The whole growth process was performed under a strongly reducing atmosphere maintained by a graphite heating element.

Subsequently, studies were performed on plate samples of 0.6 mm thickness, cut from the as-grown Al $_2$ O $_3$ crystals perpendicularly to the growth axis and polished on both sides. The absorption spectra in the range of 190–1900 nm were recorded using a V-570 UV/VIS/NIR spectrophotometer. The samples were then irradiated at room temperature by a ^{60}Co gamma source (average gamma energy 1.25 MeV) up to an absorbed dose of 2×10^7 rad with dose rate of about 170 Gy min $^{-1}$. The TL glow curve measurements were taken over the temperature range RT to 700 K by an FJ-427A TL spectrometer with heating rate of 2 K s $^{-1}$.

2 Results and discussion

2.1 Color centers concentration of the TGT-Al $_2$ O $_3$

Figure 1 shows the absorption spectrum of TGT-Al $_2$ O $_3$ crystals. According to previous studies [11], the absorption

band at 204 nm is ascribed to F centers, whereas those at 232 and 255 nm are ascribed to F^+ centers. A comparison between TGT-Al $_2$ O $_3$ and CZ-Al $_2$ O $_3$ (inset in Figure 1) shows that the main difference is the prominent 204 nm absorption band that appears in the former but not the latter. V -type centers cannot clearly be seen from the absorption spectrum due to low concentrations. To calculate the F -type color center concentrations of these crystals, we need to know the parameters describing each band. The observed spectra show that the 204, 232, and 255 nm bands are superimposed on one another. To accurately separate the spectrum into different bands, it is essential to know the precise shape of each band at the temperature of the sample during the absorption measurement. The absorption bands observed so far are Gaussian, or very nearly so, but in resolving spectra into component bands these are assumed to be purely Gaussian. With that assumption, the absorption spectrum is resolved by Gaussian fitting into three bands centered at about 204, 232, and 255 nm.

A well-known relation, the Smakula formula, exists between the density of the absorption centers and the parameters of the absorption bands. For Gaussian lineshapes, the relation becomes [12]

$$N = 0.87 \times 10^{17} KW \left[\frac{n}{(n^2 + 2)^2} \right] / f_0, \quad (1)$$

where N (cm $^{-3}$) is the concentration of color centers, K the value of the absorption coefficient at the band maximum, expressed in cm $^{-1}$, W the full width at half maximum of the absorption band, expressed in eV, n the crystal refractive

Figure 1 Absorption spectrum of TGT-Al $_2$ O $_3$ crystals.

index for the wavelength corresponding to the maximum of the absorption band, and f_0 the oscillator strength for a given transition. The scatter of the refractive index of Al_2O_3 single crystals is described as [13]

$$n^2 - 1 = \frac{A_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{A_2 \lambda^2}{\lambda^2 - \lambda_2^2} + \frac{A_3 \lambda^2}{\lambda^2 - \lambda_3^2}, \quad (2)$$

where $\lambda_1 = 0.06144821$, $\lambda_2 = 0.1106997$, $\lambda_3 = 17.92656$, and the A 's are fitting constants taking values $A_1 = 1.023798$, $A_2 = 1.058264$, $A_3 = 5.280792$. Using these parameters, we calculate refractive indices for the various bands: $n = 1.90418$ for the 204 nm band, $n = 1.86294$ for the 232 nm band, and $n = 1.84116$ for the 255 nm band. The total oscillator strength of the F^+ centers for unpolarized light is $f_{F^+} = 0.66$ [14] and $f_F = 1.3$ was estimated by Evans [15]. The parameters K and W were obtained from curve fitting of the absorption spectra. The spectrum parameters and the calculated results, listed in Table 1, indicate that the concentration of the F -type color centers is high.

2.2 Trap parameter calculation

A typical TL glow curve (Figure 2) for TGT- Al_2O_3 , resulting from γ -irradiation at room temperature, features a single prominent glow peak at 450 K that appears to be of first order. To know the precise trap parameters, i.e. activation energies E and frequency factors s , we first evaluated their approximate values by following two methods. Thermal activation energies E for the 450 K peak were determined using the initial-rise method as described by Garlick and Gibson [16]. Accordingly, the rise in the measured intensity I as a function of temperature in the initial rise range is very close to exponential; thus,

$$I(T) = C \exp\left(-\frac{E}{kT}\right). \quad (3)$$

By plotting $\ln I$ as a function of $1/T$, we expect a straight line with slope $-E_T/k$. Thus, from Figure 3, the activation energy E_T was found to be 0.85 eV.

The frequency factor s was calculated from the expression [17]

$$s = \left(\frac{\beta}{k}\right) \left(\frac{E}{T_m^2}\right) \exp\left(\frac{E}{kT_m}\right), \quad (4)$$

where β is the heating rate, k Boltzmann's constant, E the

Table 1 Color center concentrations and parameter values used in calculations

Band (nm)	K (cm^{-1})	W (eV)	n	f_0	N (cm^{-3})
204	54.449	0.621	1.90418	1.3	1.361×10^{17}
232	4.4622	0.268	1.86294	0.66	0.098×10^{17}
255	5.1587	0.753	1.84116	0.66	0.325×10^{17}

Figure 2 TL glow curve for TGT- Al_2O_3 (dotted line) and calculated curve (solid line).

Figure 3 Initial rise of the TL intensity of Al_2O_3 crystals.

thermal activation energy (determined by initial-rise method), and T_m the temperature at glow peak maximum. Using this relation, the frequency factor for the 450 K peak was determined to be $2.75 \times 10^{10} \text{ s}^{-1}$.

In the first-order kinetic model provided by Randall and Wilkins [18,19], E and s describe a single trapping level. The model gives for the luminescence intensity $I_{TL}(T)$ the expression:

$$I_{TL}(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \times \exp\left(-\frac{S}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{k\theta}\right) d\theta\right), \quad (5)$$

where n_0 is the initial concentration of filled traps at $t=0$, k the Boltzmann constant, β the linear heating rate, and θ a dummy variable representing temperature. A reasonably good approximation can be made for the integral appearing in eq. (5). Keating [20] used an approximation based on the first two terms and related to a temperature-dependent pre-exponential factor

$$\int_{T_0}^T \exp\left(-\frac{E}{k\theta}\right) d\theta \approx \frac{kT^2}{E} \left(1 - \frac{2kT}{E}\right) \exp\left(-\frac{E}{kT}\right). \quad (6)$$

Eq. (5) now becomes

$$I_{\text{TL}}(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \times \exp\left(-\left(\frac{s}{\beta}\right) \frac{kT^2}{E} \left(1 - \frac{2kT}{E}\right) \exp\left(-\frac{E}{kT}\right)\right). \quad (7)$$

Using eq. (7) and parameter values $E=0.85$ eV and $s=2.75 \times 10^{10} \text{ s}^{-1}$ estimated above, the calculated glow curve was repeatedly fitted until it matched the experimental data curve (solid line in Figure 2). The parameters obtained are listed in Table 2.

2.3 TL process analysis and kinetic model

The match between the fitted curve and the experimental data is very good, indicating that TL is in this instance a good first-order process. To provide a simple theoretical description, we assume a model consisting of one radiative recombination center R_m far from the valence band (VB) and one electron trap T_n near the conduction band (CB). The model is depicted in Figure 4. The recombination centers can be impurity centers; Xu et al. [10] showed, by glow-discharge mass spectroscopy analysis, that impurity concentrations for Si, Cr, Fe, and Nb are about 8–20 ppm in TGT- Al_2O_3 . Calculations in subsection 3.1 show that the F and F^+ center concentrations are high of order 10^{17} cm^{-3} . In addition, according to our previous study [21], the concentration of the V -type centers is very small. Impurities such as Cr^{3+} or Fe^{3+} existing in the crystal would also form electron traps after γ -irradiation. Therefore, we presume traps in the model to be electron traps.

The irradiation generates instantaneously CB electrons and VB holes in the Al_2O_3 crystals. These holes are then captured by impurity recombination centers and/or some nonradiative recombination centers whereas electrons are

Figure 4 First-order kinetic TL model of Al_2O_3 crystals.

Table 2 Trap parameters obtained by fitting experimental date

Glow peak max. (K)	Activation energy (eV)	Frequency factor (s^{-1})	Heating rate, β (K s^{-1})
450	0.94456 ± 0.00545	5.8703×10^{11}	275.15

caught in the electron traps. On heating the crystals, these trapped electrons are thermally released into the CB and can recombine with the impurity-trapped holes. The possible retrapping of the excited electrons is assumed to be negligible. Applying the quasiequilibrium assumption

$$\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right|, \left| \frac{dm}{dt} \right|, \quad (8)$$

where n_c is the number of CB electron, n the number of trapped electrons, and m the number of trapped holes, leads to

$$I_{\text{TL}} = -\frac{dn}{dt} = ns \exp\left(-\frac{E}{kT}\right). \quad (9)$$

Upon integrating from $t=0$ to t , using a constant heating rate $T=T_0+\beta t$, we obtained the well-known Randall-Wilkins first-order expression, as given in eq. (5).

From the results and the theoretical analysis presented, there appears just one deep trap existing in TGT- Al_2O_3 under strongly reducing atmosphere. Cook et al. [7] studied low-temperature TL (ltTL) of Al_2O_3 in the range 10 to 300 K, using X-ray and UV irradiation, and observed 60 K ($E=0.17$ eV), 100 K ($E=0.22$ eV), and 220 K ($E=0.56$ eV) peaks that arise from thermal release of trapped holes from F -type centers. In addition, 260 K ($E=0.72$ eV) and 290 K peaks attributed to thermal-released electrons from F^+ -type centers are also observed. The work of Cook indicates that the F - or F^+ -type centers are shallow traps and mainly attributable to ltTL. Turner et al. [9] studied V -type centers in Al_2O_3 after γ -irradiation and attributed an absorption band at 3316 cm^{-1} to V_{OH} centers. The TL peak at 443 K results from the capture of released holes at Cr^{2+} to form Cr^{3+*} in an excited state that formed during the annealing process. This 443 K peak is very close to our 450 K peak. Based on the above results, along with the relatively high concentration of Cr^{3+} in TGT- Al_2O_3 , it is probable that the 450 K peak can be associated with Cr^{3+} impurities. Unfortunately, we could not investigate the TL emission spectra due to limitations of the TL apparatus. For the moment, the conclusions drawn are necessarily speculative.

3 Conclusions

Color center concentrations for TGT- Al_2O_3 crystals are quite different from those for CZ- Al_2O_3 . From Gaussian fitting of the absorption spectrum, calculations of concentrations were obtained using Smakula's formula. The con-

centrations for F and F^+ centers at 204, 232, and 255 nm were determined to be 1.361×10^{17} , 0.098×10^{17} , and $0.325 \times 10^{17} \text{ cm}^{-3}$, respectively. The TL glow curve exhibits a prominent 450 K peak and the trap parameters ($E=0.94456 \pm 0.00545 \text{ eV}$ and $s=5.8703 \times 10^{11} \text{ s}^{-1}$) have been calculated using the first-order kinetic equation. A simple model was presented to provide a theoretical explanation of the TL process. We suspect that the 450 K peak may be due to Cr^{3+} impurities, hence the results need further substantiation.

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