Ion beam induced luminescence studies of LiAlO$_2$ using negative ions

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HIGHLIGHTS

- Ion beam induced luminescence measurement from LiAlO$_2$ using negative ions is firstly carried out.
- F$^+$, F and F$_2$ centers emission intensity keeps decreasing with the increase of fluence.
- The intensity of F$_n$ center emission grows obviously in the early stage of irradiation and then gradually decreased to the end.
- Results obtained verify the possibility of negative ion beam induced luminescence setup for real-time monitoring of irradiation damage.

ARTICLE INFO

ABSTRACT

Lithium aluminate (LiAlO$_2$) is the candidate material for solid tritium breeder applied in the developing fusion reactors. The research of its defect behavior under ion irradiation was proceeded in the negative ions induced luminescence setup of the GIC4117 Tandem accelerator in Beijing Normal University. The ion beam induced luminescence (IBIL) measurement was performed by 20 keV H$^-$ ions at room temperature. The luminescence spectra showed seven emission bands: the 4.55 eV may due to a self-trapped exciton (STE), the 4.06 eV and the 1.72 eV may due to impurity or intrinsic defect, the 3.54 eV due to F center, the 3.20 eV due to F$^+$ center, the 2.93 eV due to F$_2$ center, the 2.30 eV due to F-center aggregates (F$_n$ center), respectively. The intensity evolutions of each band with fluence were presented and the corresponding mechanisms were discussed.

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1. Introduction

Luminescence is a sensitive technology to provide information about the defect or impurities in insulator and semiconductor materials, and the detection limit can reach ppb (parts per billion) level. Luminescence induced by ion beam irradiation is usually named Ion beam induced luminescence (IBIL) or ionoluminescence (IL). In addition, compared to other luminescence measurements, the obvious advantage of IBIL is that real-time IBIL measurement can provide in-situ information of damage evolution with ion irradiation dose (Townsend et al, 2007; Townsend, 2016; Townsend and Wang, 2013).

However, up to now, most of IBIL measurements (Brooks et al, 2001; Quaranta et al, 2008; Townsend et al, 2012; Crespillo et al, 2016) have been carried out with positive ions. As the samples

for IBIL work are insulator or semiconductor, it is difficult to avoid the charge accumulation effect on the surface of samples. The charge accumulation effect may influence the intensity of incident ions and the forms of defects, which may have an impact on the luminescence measurement. In case of negative ion irradiation, both charges (incident on material surface by negative ion irradiation and released from material surface as secondary electrons) are negative, making the number of charges incoming to and outgoing from the surface well-balanced (Tsuji et al, 1998; Tsuji et al, 1997). Therefore, luminescence induced by negative ion is quite suitable for studying the irradiation damage in materials.

In the practical application, IBIL measurement had been employed in the study of irradiation damage in lithium-based materials because these materials would be interacted with ions as the role of solid tritium breeder for fusion reactors. In the meantime, some structural characterization methods (such as cathodoluminescence, SEM and XRD) had been used on lithium-based materials to study the structural changes and influence factors during the synthesis and irradiation (Mandal et al, 2010; Carrera et al, 2001; González and Correcher, 2014). The main

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irradiation defects of lithium-based materials were the anion vacancies, obtained by luminescence methods (Asaoka et al, 1992; 1991; Grishmanov et al, 1998; Grishmanov et al, 1997a; Moritani and Moriyama, 1997). Unlike the anion vacancies, the defects connected with basic cations were seldom discussed and studied in existing literatures (Holston et al., 2015a, 2015b). In all of these materials, $LiAlO_2$ has good performances in materials compatibility, stability under irradiation, thermal conductivity and lithium oxide vapor pressures (Johnson et al., 1998; Billone et al., 1993). Nevertheless, the IBIL measurement of $LiAlO_2$ (Asaoka et al., 1992) had been carried out only once, using positive ions. Furthermore, only the defects related to single oxygen vacancy were determined and the luminescence measurement under high fluence had not been carried out yet. Therefore, it's necessary to conduct the more fundamental researches, such as negative ion beam induced luminescence measurements, to study the detailed defect behaviors under ion irradiation which may be conducive to clarify the irradiation damage caused by secondary ions in fusion reactor.

In this study, at the negative ion beam induced luminescence setup of GIC4117 tandem accelerator of Beijing Normal University, in-situ luminescence measurements from γ-$LiAlO_2$ under 20 keV H^- irradiation were carried out. The reliable spectra without the charge-up of the samples were obtained to study the damage processes during the negative ion irradiation.

2. Experiment

Based on the original negative-ion implantation system at the GIC4117 tandem accelerator of Beijing Normal University, the negative ion beam induced luminescence setup was built. A schematic diagram of this IBIL set-up was given in Fig. 1. Negative ions were produced by the GIC860A Cs sputtering negative ion source. The ion beam was deflected by two $45°$ analyzing magnets. For collecting more photons, the angle between ion beam and the surface of sample was $45°$ and the optical fiber (diameter 600 μm) was perpendicular to the surface of sample. We have used an Ocean Optics spectrometer (QE PRO) for IBIL work. The available wavelength covers range of 197−982 nm with an entrance slit size of 100 μm.

Pure single crystals of γ-$LiAlO_2$ (10 × 10 × 0.5 mm, <100> orientation), polished on the incident face, were purchased from MTI Corporation (KJ Group, China). The sample was irradiated by 20 keV H^- at room temperature. The beam current was about 900 nA with a diameter of 8 mm and beam current was measured by a Faraday cup before irradiation. The integration time was selected as
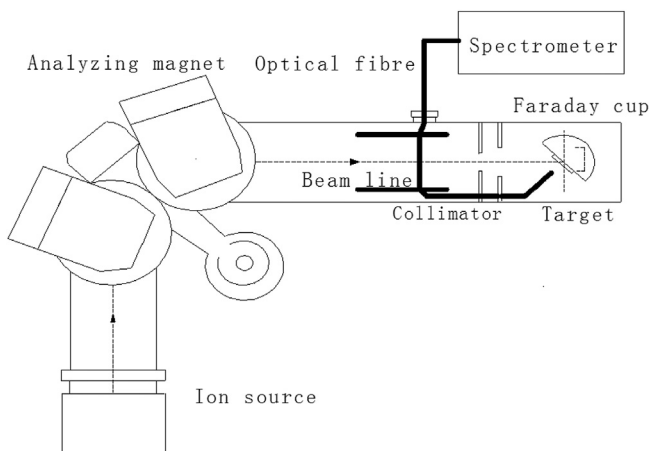
5 s for alone of the spectra and 100 continuous spectra were collected. The total irradiation dose was about 5.6×10^{15} cm^{-2}. During the irradiation, the vacuum in the chamber was kept below 3×10^{-6} torr.

3. Result and discussion

3.1. Experimental result

Fig. 2 shows the intensity evolution of wavelength spectra with fluence. It is obviously that the intensity around 540 nm increased at first and then decreased tardily. The intensities ranging from 250 nm to 450 nm showed a quick attenuation.

To proceed to more quantitative materials science, the spectra data has been transformed into the energy domain (i.e. from wavelength (λ) signals of I (λ) dλ versus λ to the energy view of I (E) dE versus E) as only from this view point can make the deconvolution fits of signals. The conversion of the wavelength axis into terms of energy is uncomplicated ($E = hc/\lambda$). However, a correct transformation for the intensity axis has been made use of the intensity correction from wavelength to energy units of ($I(E) = I(\lambda)$ $*hc/E^2$) (Townsend and Wang, 2013; Crespillo et al., 2016; Wang and Townsend, 2013).

Fig. 3 shows five IBIL spectra from $LiAlO_2$ under 20 keV H^- irradiation at room temperature with the fluences of 5.6×10^{13}, 1.7×10^{14}, 5.6×10^{14}, 1.7×10^{15} and 5.6×10^{15} cm^{-2}, respectively. A broad emission band was observed ranging from about 1.5 eV to 5e V. During the H^- irradiation, the emission band centered 2.3 eV showed an obvious growth initially and then gradually decreased to the end. The broad emission band ranging from about 3 eV to 5 eV continually decayed to nearly disappear in the end of measurement. In the last stage of the measurement two luminescence peaks centered at about 1.7 and 2.3 eV can be clearly observed with a weak intensity.

3.2. Discussion

As the spectra show an obvious overlap, Gauss fitting function has been applied to find the overlapping components. Seven peaks centered at 1.72, 2.30, 2.93, 3.20, 3.54, 4.06 and 4.55 eV are fitted as shown in Fig. 4.

Referring to the present studies about the luminescence centers in $LiAlO_2$, Li_2O and other lithium based oxides (Asaoka et al, 1992; 1991; Grishmanov et al, 1998; Grishmanov et al, 1997a; Moritani and Moriyama, 1997), the emission band centered at 2.30 eV which existed obviously from start to finish was associated with the F center aggregates (F_n center) (Grishmanov et al., 1998). The F_n center was also reported in the luminescence measurements of Li_2O, Li_2TiO_3, Li_2ZrO_3 and Li_2SnO_3 (Moritani and Moriyama, 1997). The 2.93 eV band was due to F_2 center (Grishmanov et al., 1997a; Moritani and Moriyama, 1997). The peaks centered at 3.20 eV and 3.54 eV can be related to F^+ type center (oxygen vacancies with one trapped electron) and F type center (oxygen vacancies with two trapped electrons), respectively (Asaoka et al., 1991, 1992). The previous studies about 4.06 eV band were insufficient, suggested to impurity or intrinsic defect (Asaoka et al., 1991; Grishmanov et al., 1998). The 4.55 eV band may be assigned to the recombination of STE as well as several similar observations in other lithium based oxides (Grishmanov et al., 1997b, 1998; Moritani and Moriyama, 1997), but up to now a well defined origin of this band is still to be established. A weak unreported emission band centered at 1.72 eV was observed in this work, which may be due to original impurity Ti^{3+} ($^2E \rightarrow ^2T$) or Cr^{3+} ($^2E_2 \rightarrow ^4A_2$) similar in Al_2O_3 (Crespillo et al., 2016; Molnár et al., 2001).

Fig. 5 shows the evolution of the decomposed emission bands intensities as a function of fluence. We can find that the 2.93, 3.20,

Fig. 1. Schematic diagram of the IBIL set-up.