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Studies of defects in photonic materials

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ABSTRACT

Indium tin oxide (ITO) films have high optical transmission and infrared reflectance, good electrical conductivity, excellent substrate adherence, hardness and chemical inertness. These properties lead to many applications in the area of photonics. Bombardment of ITO films with 1 MeV protons has been carried out resulting in an observed darkening. Insights into the darkening mechanism that consists of three growth stages as a function of fluence are provided by a study of the optical absorption and X-ray lattice parameter. A new interpretation is provided for the darkening mechanism in terms of the production of defect clusters resulting from the atomic displacements during implantation.

CsI crystals are very effective scintillator materials for particle detectors in high energy physics. Although radiation hard, radiation damage produces colour centres in CsI that reduce light emission and can negatively affect the luminescent centres. Using a combination of Raman and optical absorption spectroscopy applied to CsI crystals bombarded with 1 MeV protons at 300 K, the resulting defects are shown to be *F*-type centres and interstitial *V*-centres having the I_3^- structure and being responsible for absorption bands at 2.7 and 3.4 eV. Isochronal and isothermal annealing experiments show a mutual decay of the *F* and *V*-centres. The results are discussed in relation to the formation of interstitial iodine aggregates of various types in alkali iodides.

1. Introduction

Photonic materials are of major importance in many branches of science and engineering. The present work reviews progress in understanding the role of radiation induced defects in two such materials, namely indium tin oxide (ITO) and caesium iodide (CsI) that have specialist applications.

Indium oxide I_2O_3 when doped with Sn forms the material indium tin oxide (ITO) [1]. Applications include coatings on solar collectors, energy-efficient windows on buildings, flat panel display electrodes and transparent conducting electrodes on solar cells [2]. An ITO sample for solar energy applications has a transmittance of ~80% in the visible region of the spectrum being characterised by two transmittance limits, the interband transitions at short wavelengths and at long wavelength by the concentration of free carriers. Ion bombardment of ITO films has been shown to result in darkening accompanied by increases in resistivity, but the mechanism responsible has not been previously identified. ITO is radiation hard at low fluences with little darkening, but at high fluences the darkening is more rapid [3,4]. The present work reviews new insights into the darkening mechanism in terms of the development of defect clusters [5].

The mechanism of irradiation damage and the resulting defects in alkali halide crystals have been subject to a large number of studies; these have been restricted in the main to compounds having the f.c.c. NaCl structure [6,7]. The simple cubic (s.c.) alkali halides have been rather neglected in this context, but relatively recently pure CsI has received increased interest, mainly as a result of its success as a fast scintillator in electromagnetic calorimeters for high energy physics experiments [8–13]. CsI has the advantage having high efficiency and high density leading to a small radiation length as well as being radiation hard, even in the high radiation environments encountered. Indeed, early work indicated extreme resistance to defect production by X- and ^{60}Co γ-ray irradiation [14,15] and success was only achieved in later work with high radiation flux γ-ray doses [16] and high energy charged ions [9,11,12].

The spectra and decay times of the 4.3 and 3.7 eV luminescence bands associated with the self-trapped excitons (STE's) have been studied by Nishimura et al. [17]. They depict the on-centre and off-centre configurations of the STE's in the s.c. structure that are analogues of those in f.c.c. structured alkali halides. These suggest that the radiation damage process would be excitonic in nature and that the primary defects would be *F* centres and *H*

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centres. In spite of the practical usefulness of CsI, and the appreciation that the defects produced in sufficiently high radiation environments negatively affect the luminescent centres and reduce light emission [12], in depth studies of their structures have been limited, in most cases being restricted to the measurement of *F* centres. The present work reviews new information on the production and annealing of both halogen vacancy and halogen interstitial defects in CsI [18] of relevance to its applications as a scintillator. The techniques involve a combination of Raman and optical absorption spectroscopy which have proved most successful in studies of the radiation induced defects in the f.c.c. alkali iodides [19–24].

2. Experimental

2.1. Indium tin oxide (ITO)

ITO films having a thickness of 610 nm were prepared from a target with composition 10 wt% SnO_2 and 90 wt% I_2O_3 and deposited on 2 mm thick float glass substrates. The samples were bombarded with 1 MeV protons within the fluence range 1×10^{15}–$250\times10^{15}\,cm^{-2}$ near room temperature (RT) and 373 K, respectively. Optical transmission and absorption measurements were made at RT after the proton bombardments and at chosen intervals thereafter. The optical absorption of the glass substrate was essentially unchanged after proton bombardment.

Complementary X-ray diffraction studies were performed on the samples irradiated at RT. The four main diffraction peaks from the planes (2 2 2), (4 0 0), (4 4 0) and (6 2 2) of the I_2O_3 lattice were studied.

2.2. Caesium iodide (CsI)

Randomly oriented samples of approximate dimensions $8\times8\times2.5\,mm^3$ were cut from a nominally pure CsI crystal boule and surfaces mechanically polished to a finish of 1 μm. They were bombarded by 1 MeV protons at 300 K, care being taken to minimise beam heating effects, and subsequently stored under high purity argon gas at a temperature below 273 K.

The irradiated samples were mounted in a micro-cryostat permitting optical absorption and Raman measurements. The optical absorption studies were carried out at either 80 or 300 K. Raman measurements were performed at 77 K with a low laser beam power of 1.5 mW on the sample to avoid optical bleaching of the colour centres.

Optical absorption and Raman spectroscopy were used to study the effects of isochronal and isothermal annealing of the irradiated samples. The results were analysed by the procedures of Ref. [23] to determine the reaction order and activation energy.

3. Results and discussion

3.1. Indium tin oxide (ITO)

SRIM2003 simulations of the electronic and nuclear energy loss, ion range distribution and the vacancy concentrations for the proton bombardment were carried out for ITO. Owing to their limited thickness, the protons pass through the ITO films and are brought to rest within the float glass substrates. While the electronic stopping is dominant, and nuclear stopping is very small throughout the films, at the higher fluences there will be substantial vacancy concentrations created by nuclear collisions. The resulting defects are likely to contribute significantly to the overall optical effects observed.

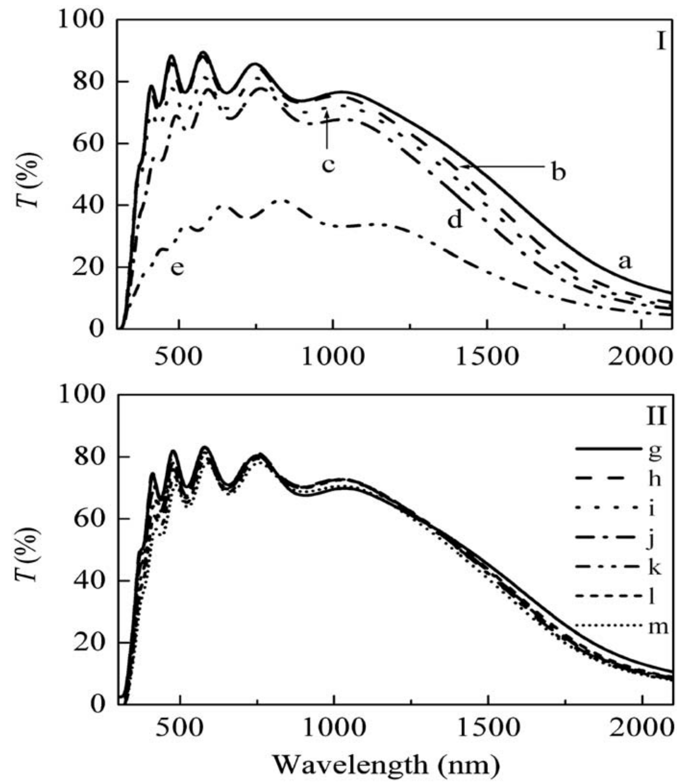

Fig. 1. Transmission spectra of selected ITO samples as a function of wavelength resulting from 1 MeV proton bombardment with increasing fluence. I shows results for RT irradiations (a: unirradiated; b: 1×10^{15}; c: 6×10^{15}; d: 40×10^{15}; e: 250×10^{15} ions/cm^2). II shows results for irradiations at 373 K (g: unirradiated; h: 6×10^{15}; i: 40×10^{15}; j: 120×10^{15}; k: 190×10^{15}; l: 215×10^{15}; m: 250×10^{15} ions/cm^2).

Fig. 1 shows the changes in the optical transmission of the ITO films over a wide wavelength range as a function of 1 MeV proton fluence at RT (I) and 373 K (II). By comparison of the spectra of the unirradiated samples of ITO with the simulated spectra of Hamberg and Grandqvist [2] the free electron density of the present samples is estimated to be $8\times10^{20}\,cm^{-3}$.

In the case of the RT bombarded samples, the transmittance reduces with increasing fluence over a broad range of wavelengths. A near 40% decrease in transmittance has occurred at the highest fluence of 250×10^{15} ions/cm^2 corresponding to obvious darkening of the sample. For the 373 K bombardment there are only small decreases in the transmission even for the highest fluence.

Following storage of the irradiated ITO films for a month at RT there were only small changes in transmission for samples irradiated within the fluence range 1–$40\times10^{15}\,cm^{-2}$ but a significant recovery for the sample bombarded with fluence $250\times10^{15}\,cm^{-2}$.

Complementary X-ray diffraction studies over the same fluence range were performed on the samples immediately after irradiation at RT and a month later. Examination of the four main diffraction peaks of the I_2O_3 lattice from the planes (2 2 2), (4 0 0), (4 4 0) and (6 2 2) confirmed that the crystalline structure of I_2O_3 was preserved. The lower fluence samples had essentially similar X-ray diffraction patterns as the unirradiated sample, but at the highest fluences namely 40×10^{15} and $250\times10^{15}\,cm^{-2}$, small decreases in the peak angles and increases in the *d*-spacings occurred. In the case of the highest fluence sample there was a significant reduction in the X-ray diffraction peak intensity. After storage at RT for one month, this sample displayed a recovery of