THE BEHAVIOUR OF Mn ATOMS IMPLANTED INTO Na^+– BETA– ALUMINA SINGLE CRYSTAL

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ABSTRACT

Upon heating, Mn atoms implanted into Na^+ – beta– alumina diffuse inwards and outwards with an activation energy of 0.96 eV, and substitute for Al^{3+} in the spinel layers of the crystal. For specimens annealed at 900°C, the optical absorption shows remarkable change in 190nm—400nm wavelength region. They fluoresce brightly green and a well– defined peak (at 525 nm) has been found in the radiative spectra.

Key words: Beta– alumina Diffusion Luminescence Ion implantation

I . INTRODUCTION

The incorporation of additives or impurities not only affects the ionic conductivity and stability of Na^+ – beta– alumina commonly used as a solid electrolyte with good performances, but also changes many of the physical and mechanical properties of the material. Li^+ and Mg^{2+} can substitute for Al^{3+} ions in the spinel– like layers of β – and β''– alumina. The substitution gives rise to an increase of ionic conductivity and an improvement of microstructure stability[1]. Lanthanide elements can exchange rapidly with Na^+ ions in the conduction layers of β''– alumina, and the resultant lanthanide β'' – alumina shows attractive features in fluorescence[2]. It is known that the incorporation of Mn^{2+} can induce a β''– phase with high ionic conductivity and stabilize the structure of β – alumina[3], and that Mn^{2+} goes to different crystallographic sites upon doping method and annealing procedure[4].

Since ion implantation can introduce virtually any ions into crystallographic sites that are not accessible by thermal methods, and the implanted ions concentrate at such a depth that can easily be studied by means of various surface analysis techniques, ion implantation would be a valuable tool to understand the basic aspects of foreign atoms in β – alumina and their effects on the properties of the material.

This paper will report the behaviour of Mn atoms implanted in Na^+ – beta– alumina single crystal and its effects on the optical properties of the material.

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Ⅱ. EXPERIMENTAL

Specimens were cleaved from a Na^+ – beta– alumina single crystal rod along the direction perpendicular to <0001> axis. Before implantation, the specimens were cleaned and annealed at 450°C for one hour in vacuum. 120 keV Mn^+ was implanted with a dose ranging from 0.5×10^{17} to 2×10^{17} cm^{-2}. A battery– powered filament was used to spray electrons onto specimen surface during implantation and RBS analysis, thus preventing the damage of electronically insulating beta– alumina crystal from the surface charging and discharging.

Thermal annealing was carried out in a quartz tube furnace pumped down to 1×10^{-4} Pa. Optical absorption spectra were recorded at room temperature with an UV - 365 spectrophotometer, the wavelength was scanned from 190nm to 700nm. Radiative spectra were taken by using a HEROS optical multichannel analyzer.

Ⅲ. RESULTS AND DISCUSSIONS

1. Implantation and annealing

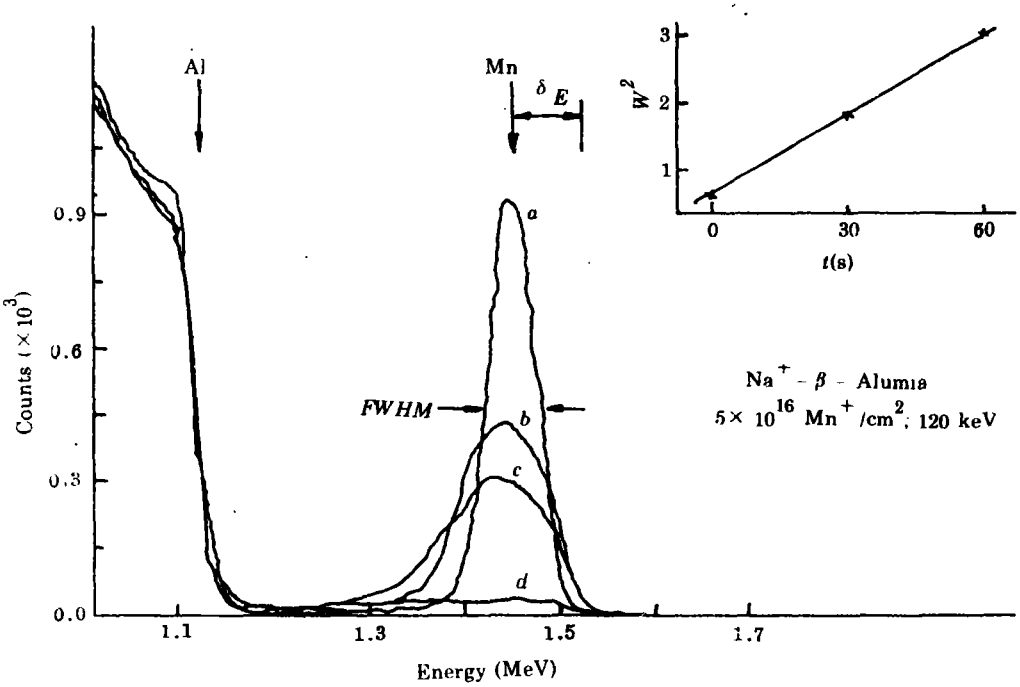

Fig.1 RBS spectra of Na^+ – beta– alumina crystal implanted with 5×10^{16} Mn^+/cm^2 at 120 keV before and after annealing at 1100°C

The probe beam is 2 MeV $^4He^+$ (*a*) as- implanted (*b*) 30 min (*c*) 60 min (*d*) 25 h

Fig.1 shows the partial RBS spectra of Mn^+ – implanted Na^+ – beta– alumina crystal before and after annealing. Mn peak is gaussian in shape. The projected range

and straggling of Mn^+ ions in beta– alumina were determined in terms of the energy shift, δE, of Mn peak position from the surface scattering and the width *FWHM* of the as– implanted peak (Fig.1 *a*). They are 76nm and 30nm respectively for Mn^+ with an energy of 120 keV. The surface energy approximation and Bragg's rule were assumed in calculating the stopping of 2 MeV He^+ in beta– alumina. The implanted dose can be estimated from the total counts under the Mn peak. In the case of Fig.1 *a*, it is 5×10^{16} cm^{-2}.

When specimens were heated at a typical temperature of 1100°C for 30 min and 60 min, Mn peak in RBS spectra spreaded out (Fig.1 *b,c*). The peak shape shows that Mn atoms diffuse simultaneously toward the interior and the surface of the specimen. The area under the Mn peaks is conserved, implying that no Mn atoms is lost from the region of observation. Annealing at 1100°C for 25 hours, Mn peak is very widly spreaded as shown in Fig.1 *d*. After increasing the temperature up to 1500°C, Mn could no longer be detected by RBS. At rather low temperatures of 700°C or 900°C, the Mn peaks remain the similar Gaussian shape.

2. Diffusion constant

Since the RBS peak for as– implanted manganese has a Gaussian shape, and it remains roughly the same shape after annealing, the concentration profiles for implanted manganese would be the same Gaussian shape. Therefore, a simplified analysis derived by S.Myers et al.[5] can be used to obtain accurate diffusion constant of Mn in beta– alumina. The equation is given by

$$[w(t)]^2 = [w(0)]^2 + 4Dt\ \ln 2$$

where $w(t)$ is the profile width, *FWHM*, at time t. $[w(t)]^2$ is displayed as a function of time in the insert of Fig.1, the slope of the plot gives the diffusion constant of Mn atoms at 1100°C to be 2.53×10^{-14} $cm^{-2}s^{-1}$.

The diffusion constant for Mn at 700°C and 900° was also found through the same procedure. The temperature dependence of the diffusion constant for Mn in beta– alumina is shown in Fig.2, the slope of the plot yields an activation energy of 0.96 eV and an equation $D = 7.91\times10^{-11}\exp(-0.96/KT)$, which governs the diffusion of Mn in beta– alumina.

This is quite different from the behaviour of Ag implanted into beta– alumina[6], where Ag atoms diffuse very rapidly with an activation energy of 0.16 eV through the vacancy clusters and also through the conduction planes of crystal between the clusters, eventually form colloidal aggregates in the crystal. In the case of implanted manganese, however, no precipitates were observed and diffusion was enhanced only by implantation induced damage.

3. Lattice location

As the implanted layer recrystallizes into small, slightly misoriented crystalline

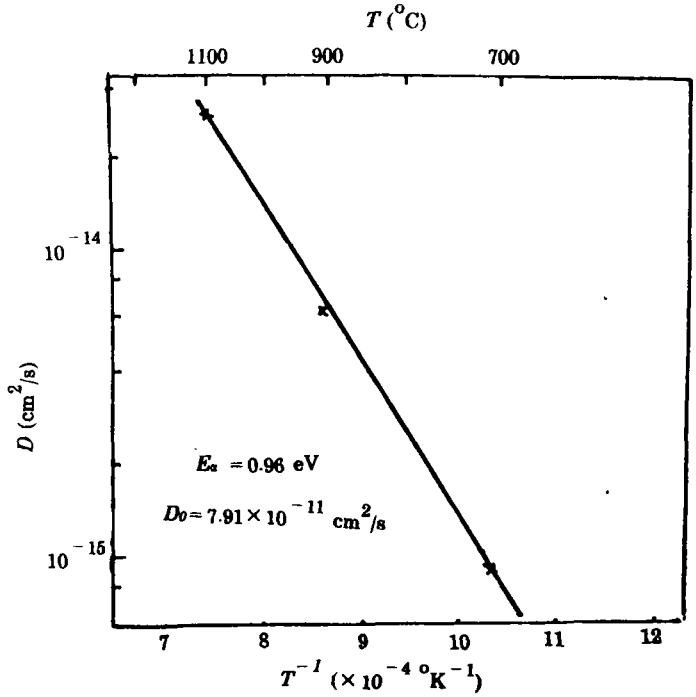

Fig.2 The temperature dependence of the diffusion constant of Mn atoms implanted into Na^+– beta– alumina crystal

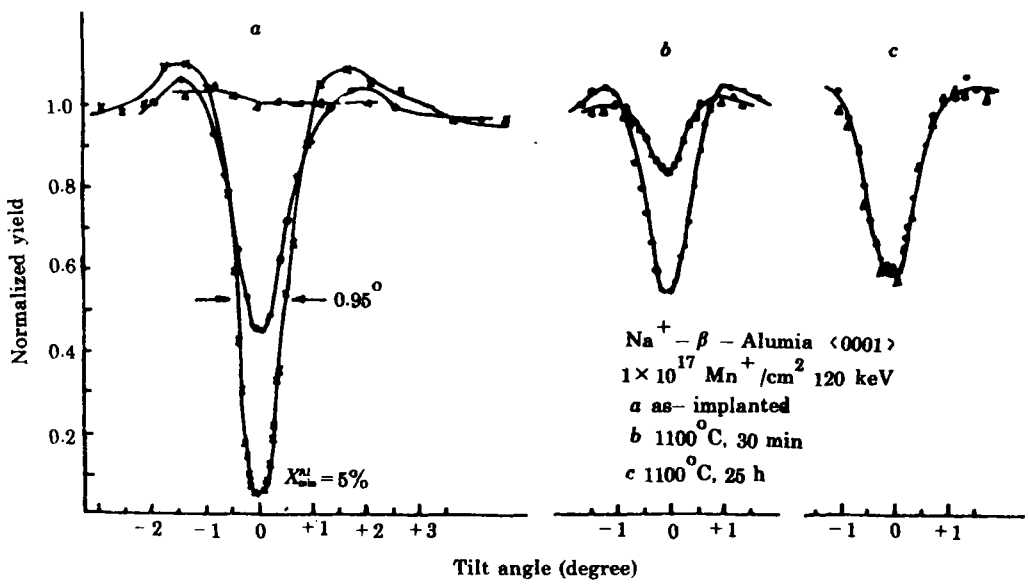

Fig.3 RBS yields as a function of angle across ′ 0001` channel

× Al yield from unimplanted crystal ▲ Mn yield

● Al yield both from implanted specimen and annealed at 1100°C

region[7], Mn atoms migrate in the lattice. The location of Mn atoms in the host

crystal can be determined by using RBS combined with channeling technique[8]. Fig.3 displays the backscattering yield as a function of angle across <0001> axial channel. It is clear that implantation damaged the host lattice (χ_{min}^{Al} = 45%) and the as- implanted Mn atoms are randomly distributed (Fig.3 *a*). After annealing at 1100°C for 30 min, the angular scan for Mn(Fig.3*b*) showed a dip of χ_{min}^{Mn} = 85%, indicating that some of the Mn atoms have been arranged in order. When the specimen was heated at 1100°C for 25 hours, the angular scan for both Mn and Al atoms are identical (Fig.3 c). For the direction perpendicular to the <0001> axis, there existed the similar results. From channeling viewpoint, these suggest that almost all Mn atoms have substituted for Al^{3+} in the spinel layers of the crystal. The conclusion is consistant with the one derived from EXAFS measurement.[9]

4. Optical absorption and radiation

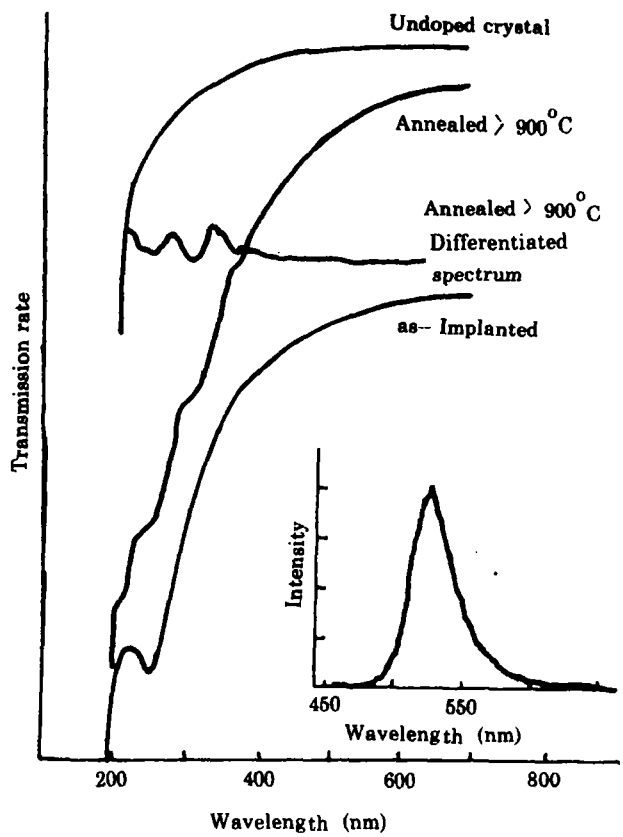

Fig.4 Optical absorption and radiation spectra of Na^+ - beta- alumina implanted with 1.2×10^{17} Mn^+/cm^2 at 120 keV

For specimens annealed at 900°C for more than 30 min, the optical absorption

spectrum showed remarkable change in the wavelength region from 190 nm to 400 nm (Fig.4), implying that new energy levels have been generated in the wide energy gap (6.53 eV) of beta– alumina crystal. Under UV or X–ray excitation, such specimens fluoresce brightly green, and decay very slowly after excitation. The radiative spectra give a well–defined peak in 500nm to 550nm region (the insert in Fig.4). For specimens annealed at 700°C, only F–center band was found in the absorption spectra, and rather weak redish yellow luminescence was detected.

This is also different from silver implantation in beta– alumina crystal, where the strong absorptions at 414nm and 250nm band characterize the colloidal Ag particles and F–centers respectively, and no fluorescence was reported[6]. For implanted Mn atoms, we believe that it is these metastable levels in the energy gap that are responsible for the bright fluorescence under certain excitation.

Although further studies are undertaking in order to determine the valence state of the implanted Mn atoms after annealing and the details of the related electron transitions, the reproducible luminescence of this type suggests that the large, clear and chemically stable beta– alumina crystal can be an attractive host for studying the transfer of radiant energy and for developing new laser, phosphor or optoelectronic materials.

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