CHAPTER 4

EFFECT OF 120 MeV Ag\textsuperscript{9+} IONS IRRADIATION ON YCOB SINGLE CRYSTALS

4.1 ION IRRADIATION: AN INTRODUCTION

Several interesting and advantageous properties of matter in the solid state are related to the presence of defects and impurities. The imperfections in solids are exploited for employing them in various applications. In the growth of single crystals for technological applications, the defects are introduced either by varying the growth parameters or by intentionally adding impurities during the crystal growth process. The defects can also be introduced in the crystalline solids by means of ion irradiation. In semiconductor industries, ion beam processing is itself an integral part of device fabrication. The defects in perfect solids may be considered as a perturbation in the local symmetry around the atoms. In general, defects in crystalline solids are classified as point defects, line defects, plane defects and volume defects. They can arise due to chemical impurities, interstitials, vacancies, vacancy-impurity complex or due to internal surfaces, glide planes, dislocations and grain boundaries.

4.1.1 Energy Loss and Damage

After penetrating inside materials, ions lose their kinetic energy through collisions with (1) nuclei, (2) bound electrons of the target atoms and (3) free electrons inside the target material. Ions penetrate some distance
inside the material until they stop. In case of high energy ions, the ions slow down mainly by electronic energy loss in the beginning of the ‘slowing down’ process and they move atoms in a straight path. When the ions are slowed down sufficiently, the collision with nuclei (the nuclear stopping) become more and more probable, and eventually ions are stopped by nuclear scattering. When atoms of the solid receive significant recoil energies they are removed from their lattice positions and produce a cascade of further collisions in the material.

The calculation of range requires the knowledge of the rate of energy loss of the ions. According to the classical scattering theory, the interaction of the moving ions with the target atoms is described assuming two separate processes, collisions with nuclei and collision with electrons. The former is due to the coulomb repulsion between the ion and the target nuclei. The nuclear stopping component is usually considered separately because the heavy recoiling target nucleus can be assumed to be unconnected from its lattice during the passage of the ion. The elastic recoil energy transferred to it can be treated simply as the elastic scattering to two heavily screened particles. Excitations or ionization of electrons are only a source of energy loss and do not influence the collision geometry. This is justified if the energy transferred to the electrons is small compared to the exchange of kinetic energy between the atoms, a condition usually fulfilled in ion implantation. The ion is thus deflected by nuclear encounters and continuously loses energy to the electrons.

4.1.2 Ion Beam and Crystals

Ion beam irradiation can play an important role in the study of defects related to crystals, as controlled amount of defects can be introduced
by selecting suitable irradiation parameters. Defects like point defects and etc.
can also be selectively introduced by proper choice of ion mass and energy of
the irradiating ions.

Energetic ions of energies up to few hundred kilo electron volt (10
keV to 100 keV) have been widely used for ion implantation (Avasthi et al
2004). MeV ion implantation has attracted considerable attention in recent
years as it provides an extension of ion implantation technique with a high
potential for defect engineering and modification of solid materials. Extending
the ion energy from keV to MeV provides many advantages in
terms of the larger ion range for deep implantation and the minimized surface
damage for modification of deeply buried layers. There are also several
interesting problems that are to be understood and solved with respect to the
mechanism of radiation damage and ion irradiation induced phase transitions.

Ion beams can be classified into three broad groups on the basis of
energy and mass of the irradiated ions.

4.1.2.1 Irradiation with low energy ions

Low energy ions in the range of 50 keV to 500 keV are extensively
used for doping in semiconductors. Low energy light ions produce point
defects and heavy ions produce extended defects in materials but range of
both light and heavy ions is very low as compared to that in case of high
energy ions.

For the last several decades, low energy ion beams have been used
extensively for the purpose of ion implantation. Ion implantation is an
essential process for the production of modern devices and integrated circuits
(IC) based on Si and compound semiconductors. In the case of III-V
compound semiconductors, there are two important applications. The first is the implantation of dopants to create n-or p-type III-V semiconductors. The second is the implantation of ions like H, He, B, O, etc to convert a doped layer to a highly resistive one through defect engineering (Ahmed et al 2001).

Ion beam interaction in semiconductors with ions having energy, such that during slowing down, the energy of the ion is dominantly lost through nuclear energy loss process is well understood. During slowing down, an ion interacts inelastically with electrons and elastically with other target atoms. If the kinetic energy, $E^1$, transferred to the host atom is higher than the displacement threshold energy $E_d$ (~8eV for Ga and ~6eV for As), the knock-on atom leaves its lattice site and depending on the residual kinetic energy, $E^1-E_d$, they can move for a certain path length. These atoms recoil and collide with other atoms giving rise to further generation of collisions which produce many low-energy recoils and induce small displacements in nearly random directions. This sequence of collisions and displaced atom multiplication is often called collision cascade and it lasts for $\sim 10^{-13}$ seconds, which is the ion range divided by the average ion velocity.

This fast process is followed by a redistribution of the energy into surrounding material by both lattice and electron conduction, and lasts for an additional time interval of $10^{-11}$ seconds, resulting in local thermal equilibrium. In the following $10^{-9}$ seconds, the unstable disorder relaxes and some ordering occurs by a local diffusion process and the system attains total thermal equilibrium.

4.1.2.2 Irradiation with swift heavy ions (SHI)

4.1.2.2.1 Irradiation with high energy light ions (HELI)

These ions are most suitable for defect engineering, since the point defects produced by these ions are almost uniformly distributed deep within
the sample and the ions get implanted at a depth of more than 100 µm. This excludes the possibility of any interference from implanted ions in modifying the material properties. In some cases, the samples can be made thinner than the range of ions where the ions pass through the samples or samples may be grown on substrates such that the range of the ions is more than the film thickness. In contrary to interaction of swift heavy ion (SHI) where electronic energy loss above threshold causes track formation, the damage accumulation by high energy light ions (HELI) is largely due to the nuclear energy loss (Kamarou et al 2006). The HELI irradiation produces point defects due to nuclear energy loss in the samples and can be estimated using Stopping Range of Ions in Matter (SRIM) calculation. Moreover, the electronic energy loss of HELI is very high compared to the nuclear energy loss but much less than the threshold energy for track formation, which can be uniquely utilized for defect engineering and material modification through ionization of inherent defects.

4.1.2.2.2 Irradiation with high energy heavy ions (HEHI)

In the slowing down process, low energy ions lose energy through nuclear energy loss process. But in the case of high energy ions, the electronic energy loss dominates over nuclear energy loss. Heavy ions lead to extremely strong electronic excitations inside a narrow cylinder around each ion path. The initial interaction processes of the energy transfer from a high energy heavy ion to electrons bound to inner shells take only $10^{-19}$ to $10^{-17}$ s and slightly longer for collective electronic excitations like the formation of plasmons (Schiwietz 2004). Hence, just after the passage of the SHI, the narrow cylindrical target zone coaxial with the ion path consists of two component plasma of cold lattice atom and hot electrons. Such a narrow region is often called as ‘ionization spike’.
High energy (with energy in MeV) ions are used to introduce buried layers in semiconductors, for their applications in the formation of gettering layers, active layer-substrate isolation, power electronics applications, etc. Recently, there has been a quantum change in the understanding of ion-material interactions and ion beam mixing, especially due to the interesting development while using high energy ions.

There is variety of reports available in literature on the effect of irradiations on several organic and inorganic single crystals. One of the interesting inorganic crystal on which the effect of irradiations are widely studied is lithium niobate (LN). Lithium niobate (LiNbO₃) is a material with outstanding properties such as, wide range of transparency, high nonlinear optical (NLO) coefficients, as well as high chemical resistance. Therefore, it is a very interesting material for the fabrication of integrated optical devices (Arizmendi 2004). For this purpose, ion beam techniques are employed as appropriate tool to change the physical properties of LN. Due to the formation of defects, a change in the refractive index is observed which is used for the fabrication of buried waveguides (Townsend et al 1994, Olivares et al 2005, Chen et al 2007). Furthermore, the chemical resistance is also reduced to a little extent. As a consequence, the damaged regions are etched in hydrofluoric solution (HF) without affecting the non irradiated crystal (Kawabe et al 1978, Destefanis et al 1979, Gotz and Karge 1983, Ashby et al 1989). In combination with selective ion irradiation using standard masking technologies the fabrication of high quality micro- and nano-structures in LiNbO₃ is achieved (Hartung et al 2008, Schrempel et al 2006).

In order to generate vertical patterns, buried damaged layers are produced using appropriate irradiation conditions. For vertical structures in the sub-micrometer range light ions (e.g. He) are being used for the irradiation to keep the surface free of defects. Unfortunately, during He irradiation
bubble formation occurs, if the irradiation is carried out at room temperature (Kling et al 2001, Roth et al 2006). As a consequence the structures are destroyed due to blistering effects. However, if the irradiation is performed at low temperatures bubble formation can be suppressed. An annealing step prior to etching is performed to reduce existing surface damage.

On doping with certain rare earth ions, LN crystals become suitable for use as optical amplifiers, and up-convertors. A laser emission around 1.5 µm which is commonly used in telecommunication (Kenyon 2002) can be achieved by doping erbium into lithium niobate. A thin surface layer of lithium niobate, containing erbium ions (Er:LiNbO$_3$), can be, in principle, fabricated in several ways (Tsonev 2008) doping during a growth process, diffusion from an erbium metal layer evaporated on the surface of an LN wafer, ion exchange from a molten erbium salt and by ion implantation is carried out widely. Erbium ions are implanted at energies between 330 and 500 keV with various fluences into LiNbO$_3$ single-crystals (Svecova et al 2009).

A few reports are available in literature on the irradiation effects on organic NLO crystals such as L-asparaginimum picrate (LASP), glycine lithium sulphate (GLS), sodium sulphanilate dehydrate (SSDH) single crystals and etc (Srinivasan et al 2007, Mythili et al 2008). The effects of SHI irradiation, like 100 MeV Ag$^{7+}$ ion irradiation of different fluences on the optical, mechanical and dielectric properties of organic single crystals were studied. The defects produced due to irradiation have been studied in detail by defect-sensitive techniques like photoluminescence (PL) and optical absorption spectra. The micro hardness of the crystals, which is attributed to the amorphization induced due to irradiation were also analysed. An increase in the dielectric constant in some cases was observed on irradiation, which is attributed to the disordering of crystal lattice by ion beams. A notable increase in the dielectric
constant is the stamp of the electro optic property of the irradiated crystals. Thus by irradiating an organic crystal suitably with optimized ions in appropriate conditions, electro-optic modulators can be effectively fabricated from them.

A few borate based crystals such as bismuth borate (BIBO) (Lei Wang et al 2008), lithium borate (LBO) (Tolga Depci et al 2008) were also subjected to ion irradiation experiments and their effects have been analyzed and reported.

YCOB single crystals are being used in applications involving high power lasers. The studies on YCOB crystals discussing its thermal robustness, good mechanical and chemical stability were performed and reported. In a demonstration experiment at Lawrence Livermore and Crystal Photonics Inc., Sanford, Florida, 50% conversion efficiency was achieved by using 450 watts of infrared light on a single YCOB crystal and green light emission with 225 watts was observed (Arnie Heller 2006). The experiment has been carried out for 30 minutes using 18,000 shots at the rate of 10 shots per second. The quality of the YCOB crystal has not degraded due to thermal effects that may have generated. The laser induced damage threshold value of the YCOB crystals is also high (2.4 GW/cm², for 1064 nm radiation, 20 ns pulse). The study on the effect of SHI irradiation was not carried out earlier on YCOB crystals. The interaction of SHI irradiation on the crystals leads to modification in the optical, mechanical and electrical behaviour of the crystals. An NLO crystal is employed in devices only when it has excellent optical properties combined with good thermal and mechanical properties. Hence, in order to study the effect of irradiation on YCOB crystals, the YCOB crystals grown from boron tri oxide flux were subjected to irradiation. There are no reports available in literature on the swift heavy ion irradiation on YCOB crystals experiments. The GAXRD, optical transmittance and photoluminescence studies were performed and their results are discussed
4.2 IRRADIATION EXPERIMENT

4.2.1 Ion Irradiation Facility

4.2.1.1 Pelletron

The Inter – University Accelerator Centre (IUAC), New Delhi has a 15 UD tandem electrostatic accelerator, capable of accelerating any ion from proton to Uranium to energies from 50 MeV to 200 MeV (Kabiraj 2007). The pelletron belongs to a class of accelerators known as tandem Van de Graff accelerator. A schematic diagram of the pelletron is shown in Figure 4.1. The pelletron with a vertical geometry is installed in a stainless steel tank, which is 26.5 m long and 5.5 m in diameter. It is filled with sulphur hexa-fluoride insulating gas at a pressure of about 6-7 bar. In the middle of the tank, there is a high voltage terminal of about 1.52 m in diameter and 3.81 m in height. This terminal can be charged to a potential from 4 to 16 MV. A potential gradient is maintained with ceramic titanium diffusion bonded accelerating tubes from high voltage to ground at the top of the tank as well as from the bottom of the tank. The negative ions are produced and pre accelerated to about 250 keV by a sputter type ion source known as MC-SNICS (Multi – Cathode Source of Negative Ions by Cesium Sputtering).

The ions of different masses are analyzed by a 90° dipole magnet called injector magnet and are turned in a vertically downward direction towards the terminal. On reaching the terminal, they pass through a stripper (C-foil or N₂ gas) that strips the ions off their electrons, thus changing them to positive ions, which are further accelerated as they proceed towards the bottom of the tank at ground potential. The final energy of the ions emerging from the accelerator is given by equation (4.1),

\[ E = \{ E_{\text{deck}} + (1+q)V_T \} \]  

(4.1)
where $V_T$ is the terminal potential in MV, $q$ is the charge state of the ion after stripping and $E_{\text{deck}}$ (few hundreds kV) is the deck potential of the MC-SNICS source. These high energy ions are analysed in energy with the help of a 90° bending magnet known as analyzer magnet and directed to the desired experimental beam line with the help of a multiport switching magnet which can deflect the beam in any of the seven beam lines in the beam hall. The whole beam line of the accelerator is in ultra high vacuum (UHV). During passage of ions through accelerator beam line, the ion beam is kept centered and focused using steering magnets and quadrupole triplet magnets. The beam is visually monitored by glow on quartz and beam profile monitors (BPM). The beam current is measured by means of Faraday cups. Irradiations were carried out on YCOB single crystals with heavy ions of 120 MeV silver ($\text{Ag}^{9+}$).

Figure 4.1 Schematic diagram of pelletron accelerator
4.2.1.2 Materials science beam line

The accelerated beam from the pelletron is brought to the beam hall and can be switched to anyone of the seven beam lines. Among them, one is the materials science beam line, which is at 15º to the right with respect to the zero degree beam line. Material science beam line has three chambers and these are connected one after another as shown in Figure 4.2. The high vacuum chamber where most of the irradiation and elastic recoil detection is carried out is made up of stainless steel. The vacuum in the chamber is created by using a turbo pump. The vacuum during the irradiation experiment is of the order of $10^{-6}$ mbar. The target ladder (containing samples mounted on it) is inserted in to the chamber.

![Schematic diagram of Materials Science beam line at IUAC, New Delhi](image)

Figure 4.2 Schematic diagram of Materials Science beam line at IUAC, New Delhi

A stepper motor in conjunction with suitable mechanical assembly is used to control the up and down motion of the ladder. This up and down
motion can also be done from the remote data acquisition room using an electronic control panel. The sample position can be aligned with respect to the ion beam by first looking at the luminescence of the beam on the quartz crystal and after that the sample is brought to the position of the quartz, by marking on the screen. The position of the quartz and samples are observed using close circuit television (CCTV) kept in data room. With the help of a magnetic quadrupole and a steerer, the beam is focused on the target. For irradiation, the beam is scanned in x-and y-direction over a maximum area of $10 \times 10 \text{ mm}^2$ with the help of a magnetic scanner. The scanning ensures the uniformity of irradiation over the whole area of the sample. A cylindrical enclosure of stainless steel (suppressor) surrounds the sample ladder, which is kept at a negative potential of 120 V. This enclosure suppresses the secondary electrons coming out of the sample during irradiation. An opening in the suppressor allows the ion beam to fall on the sample. The total number of the particles/charges falling on the sample can be estimated by a combination of the current integrator and the pulse counter from which the irradiation fluence can be measured. The irradiation experiments were performed in the high vacuum chamber, with a typical vacuum maintained at $3 \times 10^{-6} \text{ mbar}$. The reason for the vacuum environment is to avoid any collision of the particle (beam) with gas molecules. The samples to be irradiated were mounted on the four sides of the target ladder (on copper block), which are separated from each other by a distance of about 15 mm. The time or counts calculated for the desired ion fluence for each sample was calculated using the following relations (4.2) and (4.3).

$$\text{Time (T)} = \frac{F(\text{Fluence}) \times \text{Exposed area (1cm}^2\text{)}}{1.6 \times 10^{-19} \times \left( \frac{1(\text{nA})}{q} \right)}$$ \hspace{1cm} (4.2)

where, I is beam current and q is the charge state of ion.
In the present investigation, YCOB single crystals were irradiated with 120 MeV silver Ag\(^{9+}\) ions at a current density of 3 pnA/cm\(^2\) at the fluences of \(1 \times 10^{13}\), \(5 \times 10^{13}\) and \(1 \times 10^{14}\) ions/cm\(^2\) at room temperature (RT) and with \(5 \times 10^{13}\) ions/cm\(^2\) at liquid nitrogen temperature (LNT). The projected range was calculated to be 13.07 µm for the 120 MeV Ag\(^{9+}\) ions using SRIM code (Stopping and Range of Ions in Matter) (Ziegler et al 2003).

4.3 CHARACTERIZATION STUDIES

Characterization studies such as, Glancing Angle X-ray Diffraction (GAXRD), optical transmission studies (UV-VIS-NIR) and Photoluminescence (PL) measurements were performed both on the pristine and irradiated samples and were analysed.

4.3.1 X-ray Diffraction Studies

Glancing angle X-ray diffraction (GAXRD) spectra of the pristine and Ag\(^{9+}\) ion irradiated YCOB single crystals were recorded using the Bruker AXS diffractometer. The recorded spectra are shown in Figure 4.3. The peak observed at 30\(^\circ\) corresponds to the (201) peak of the pristine YCOB crystal. The XRD peak intensities were found to decrease when the ion irradiation dosage was increased. The decrease in the intensity of the dominant peak could be attributed to the creation of defects due to irradiation. The ion tracks are created from the ion-induced melt due to the mechanical stress that had arisen as a result of thermal expansion (Szenes 2002).
Figure 4.3  GAXRD spectra of (a) Pristine YCOB crystal, YCOB single crystals irradiated by 120 MeV Ag\textsuperscript{9+} ions with fluences of (b) $5 \times 10^{13}$ ions/cm\textsuperscript{2} at LNT (c) $1 \times 10^{13}$ ions/cm\textsuperscript{2} at RT (d) $5 \times 10^{13}$ ions/cm\textsuperscript{2} at RT and (e) $1 \times 10^{14}$ ions/cm\textsuperscript{2} at RT

4.3.2 Optical Transmittance Spectra

YCOB single crystals are employed in devices for the generation of high power ultra violet lasers, mainly due to the following reasons.
i. The transmission edge of YCOB crystal is at 220 nm.

ii. The YCOB crystal has higher laser induced damage threshold and is non hygroscopic.

In order to study the effect of irradiation on the optical transmission property of the YCOB crystal, UV-VIS-NIR measurements were carried out. Figure 4.4 shows the optical transmission spectra of irradiated YCOB single crystals. The cutoff wavelength for the pristine YCOB crystal occurs sharply at 220 nm. The Ag\(^{9+}\) ion irradiation at RT and LNT resulted in decreasing the sharpness of the transmission edge and the formation of additional humps in the curve. This is due to the fact that irradiation has induced lattice damage which had created defects, whose energy levels fall below the conduction band and hence the band gap has reduced.

![Optical transmittance spectra](image)

**Figure 4.4** Optical transmittance spectra of (a) Pristine YCOB crystal, YCOB single crystals irradiated by 120 MeV Ag\(^{9+}\) ions with fluences of (b) 5×10\(^{13}\) ions/cm\(^2\) at LNT (c) 1×10\(^{13}\) ions/cm\(^2\) at RT (d) 5×10\(^{13}\) ions/cm\(^2\) at RT and (e) 1×10\(^{14}\) ions/cm\(^2\) at RT
4.3.3 Photoluminescence Spectra

YCOB single crystal is wide bandgap material. The material can be used for as a tunable laser source since it emits over a broad spectral range. In order, to study the emission characteristics of the YCOB crystals upon irradiation, the Photoluminescence studies were carried out on the pristine and Ag⁹⁺ ions of 120 MeV irradiated (RT and LNT) YCOB single crystals. The recorded spectra are shown in Figures 4.5 and 4.6. As the irradiation (RT and LNT) fluences increase the intensity of the peaks decreases because of the loss of luminescent property of the material. Drastic reduction of PL intensity after irradiation was observed, as evident from the spectra recorded, which confirmed the increase of lattice damage on the surface of the sample due to high energy irradiation.

Figure 4.5 Photoluminescence spectra of pristine YCOB single crystal
Figure 4.6 Photoluminescence spectra of YCOB single crystal irradiated by 120 MeV Ag\textsuperscript{9+} ions with fluences of (a) $5 \times 10^{13}$ ions/cm\textsuperscript{2} at LNT (b) $1 \times 10^{13}$ ions/cm\textsuperscript{2} at RT (c) $5 \times 10^{13}$ ions/cm\textsuperscript{2} at RT and (d) $1 \times 10^{14}$ ions/cm\textsuperscript{2} at RT

4.4 CONCLUSIONS

YCOB single crystals grown from boron tri oxide flux were subjected to swift heavy ion irradiation studies. Silver ions (Ag\textsuperscript{9+}) with the energy of 120 MeV were employed for the present investigation. The penetration depth of the ions in the sample was calculated using the SRIM calculations. The pristine and the irradiated samples were analysed by GAXRD, UV-VIS-NIR and PL measurements. Degradation in the crystalline quality has been observed in the GAXRD measurements. The optical transmission study reveals that the sharpness of the UV absorption edge has
decreased due to the creation of defects. The photoluminescence characteristics of the YCOB crystals were recorded before and after irradiation. The pristine YCOB crystal has a broad emission spectrum centered at 560 nm. For the irradiated YCOB crystal, the PL emission curves are also centered around 560 nm only. But there is a drastic decrease in the intensity of emission on increasing the ion fluencies, which may be due to the creation of defects in the lattice present at the surface of the crystal. The crystalline quality of the YCOB crystals is affected upon irradiation and hence the suitability of YCOB crystals is once again established for opting them in devices involving high power lasers.