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INFRARED EMISSION FROM Si IMPLANTED WITH HIGH Er CONCENTRATION*

Xiao Zhi-song(肖志松)[a)†], Xu Fei(徐 飞)[d)], Zhang Tong-he(张通和)[a)],
Cheng Guo-an(程国安)[b)], Xie Da-tao(谢大韬)[c)], and Gu Lan-lan(顾岚岚)[d)]

[a)] *Key Laboratory in University for Radiation Beam Technology and Materials Modification, Beijing Normal University; Institute of Low Energy Nuclear Physics, Beijing Normal University; Beijing Radiation Center; Beijing* 100875, *China*

[b)] *Department of Materials Science and Engineering, Nanchang University, Nanchang* 330047, *China*

[c)] *Department of Chemistry, Peking University, Beijing* 100871, *China*

[d)] *Surface Physics Laboratory, Fudan University, Shanghai* 200433, *China*

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Erbium-doped silicon has been fabricated by ion implantation performed on a metal vapour vacuum arc ion source. After rapid thermal annealing (RTA), 1.54μm photoluminescence was observed at 77K. Rutherford backscattering spectrum indicated that Er ions are mainly distributed near the surface of the samples, and Er concentration exceeded 10^{21}cm^{-3}. Needle nanometre crystalline silicon (nc-Si) was formed on the substrate surface. Band edge emission spectrum at 10K verified that the minority carrier lifetime increased upon RTA. The photocarrier mediated processes enabled energy transferring from nc-Si (or c-Si) to the Er^{3+} ions and resulted in light emission of 1.54μm.

Keywords: erbium, silicon, ion implantation, photoluminescence
PACC: 6172

I. INTRODUCTION

There has been much interest in obtaining high emission from crystalline silicon through the introduction of luminescent rare-earth dopants.[1−3] Of particular interest is Er, which in its 3+ state emits at a wavelength of about 1.54μm, close to the minimum absorption of silica-based optical fibres.[4,5] Er ions are inserted in the Si matrix, and the excitation can be achieved through the carriers provided by the host, whereas the subsequent de-excitation can result in a sharp atom-like emission. In this way, light emitting Si-based devices can in principle be fabricated. However, the low solid solubility of Er in Si ($\sim 10^{16}$cm^{-3} at 1300°C)[6] prevents the incorporation of high Er concentration, even with the use of ion implantation. Er incorporation at concentrations higher than 5×10^{17}cm^{-3} was prevented by the onset of Er precipitation.[7] At present, the incorporation of erbium at concentrations higher than 10^{20}cm^{-3} (well above both solid solubility and limits set by the onset of precipitation) can be achieved by tuning nonequilibrium techniques, such as ion implantation, molecular beam epitaxy, ion-beam assisted sputtering, and chemical vapour deposition.[8−10] Moreover, a high concentration Er up to 10^{21}cm^{-3} was obtained by electrochemical doping (ECD).[11]

However, the high concentration of Er ions is not enough to cause high efficient luminescence. Another factor that should be taken into consideration is the maximum Er concentration that can be optically activated in CZ-Si. In the case of normal ion implantation (Er ion energy from 200keV–5MeV), the solid-phase epitaxy of amorphous layers containing high Er concentration produces Er segregation at the amorphous–crystalline interface during regrowth with the Er swept by the advancing interface. On the other hand, a 20nm thick disordered layer may remain at the surface. Low-energy implantation may decrease the damage and disordered layer caused by the ion bombardment. The large ion fluence and flux performed by MEVVA ion source induce temperature elevation during the ion implantation, which can cause the growth of crystals and the activation of Er ions.

In this paper, we demonstrate that ion implantation performed by MEVVA ion source is a promising technique for producing needle Si nanocrystal structures and incorporating high Er concentrations into Si. Energy transferring from nc-Si (or c-Si) to the Er^{3+} ions results in light emission of 1.54μm.

II. EXPERIMENTAL DETAILS

*Project supported by the National Natural Science Foundation of China (Grant No. 59671051)
†Corresponding author. Tel.: +86-10-62207077; Fax: +86-10-62231765; E-mail:zsxiao@263.net

Czochralski(CZ)-grown P-Si(111) was used in the experiments with an electrical resistivity of 8–13Ω·cm. The Si wafer was implanted on one side with an average energy of 108keV Er^+ ions with doses of 1×10^{16}, 5×10^{16}, 8×10^{16}cm^{-2}. The pressure during the ion implantation was $\sim 4\times10^{-3}$Pa and the ion flux was 2.5μA·cm^{-2}, with which the substrate temperature was elevated allowing for substrate annealing to occur at a lower temperature than 100°C. Samples were subsequently annealed at 900–1100°C in a flowing Ar atmosphere for 20s to form a Si nanometre structure and to excite Er^{3+} ions. Er and Si concentrations and depth profiles were measured using Rutherford backscattering (RBS) on a 2×1.7MV tandem accelerator with normal incident 2.0MeV $^4He^+$ ions and a scattering angle of 165°. Atomic force microscopy (AFM) was applied to scan the surface micrograph of annealed samples exposed in air. The scanning area is 5μm×5μm. Photoluminescence (PL) measurements were carried out using the 441.6 nm line of a He–Cd laser as the light source and a single grating monochromator. A liquid-nitrogen-cooled Ge detector was used to detect the infrared spectrum. PL measurements were performed at 77 K and the band edge emission spectrum was carried out at 10 K.

Ⅲ. RESULTS AND DISCUSSION

Figure 1 shows the RBS spectrum of Er-implanted Si substrates. We have to bear in mind that MEVVA ion source produces both single- and multiply-charged ions, with a mean charge state of 1.5–2.5, depending on the ion species. For example, the mean charge state of Er is 2.4. Implanted element concentrations and depth profiles differ from the normal high-energy and singly-charged ion implantation, which shows a distribution of a Gaussian shape. The atomic ratio of Er to Si determined by RBS is presented for annealed samples of different Er fluence. The highest Er concentration for 1×10^{16}, 5×10^{16}, 8×10^{16} Er/cm^2 implanted Si is 1.01 at%, 7.39 at% and 9.41 at% respectively. We know that the Si concentration in substrates is $\sim4.98\times10^{22}$cm^{-3}, so the Er concentration can be calculated to be 5.03×10^{20}, 3.68×10^{21} and 4.69×10^{21}cm^{-3}. With such a high Er concentration (far exceeding the solubility), the Er ions are mainly distributed at a region 35nm from the surface. This may cause Er to be energetically favourable to nucleate twins, segregate and precipitate, which will quench the luminescence.

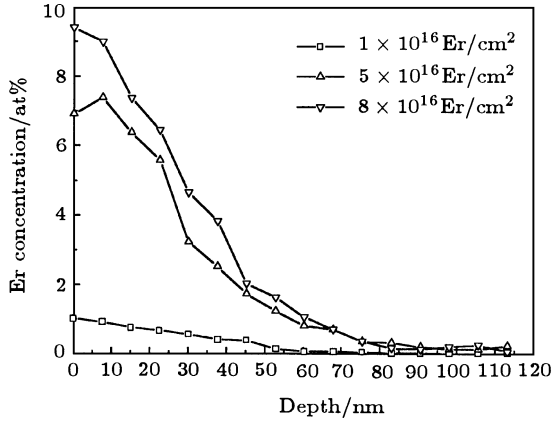


Fig.1. RBS measurement of Er concentration in CZ-Si implanted with different Er fluence.

Figure 2 shows the micrograph of single-crystalline silicon implanted with Er and annealed at various temperatures. No clear defect and displacement is observed during the as-implanted state, but small pins and holes appear on the surface. After annealing at 900°C for 20s, the defects are generated in the bulk of the substrate by displacement processes. A low-density isolated needle structure appears when the annealing temperature increases to 1000°C for 20s. X-ray diffraction and reflection high-energy electron diffraction measurements confirm that the needle structures mainly comprises crystalline Si. Upon increasing the annealing temperature, the isolated needle structures increase and link to each other, and a complete nanometre needle structure (with a diameter of about several nanometres) forms on the surface. These needles have the appearance of an extensive forest. They have very well-defined shapes that are very similar in appearance within each sample but differ in length and diameter. The length of these needles are far beyond the maximum implanted range, indicating that the formation mechanism of these structure is growth rather than sputtering and surface migration, but greatly associated with high target temperature by the self-annealing effect. Such high-density arrays of nanometre needles are interesting, as they may be potentially useful in surface applications, such as luminescence. We deduce that the growth rate is predominant at temperatures lower than 1000°C; most defects are eliminated and needle structures enlarged. If the annealing temperature continues to increase, the crystal nucleation rate will be larger than the growth rate. The nanometre needle structures will grow fast and the density will be higher than that of 1000°C,

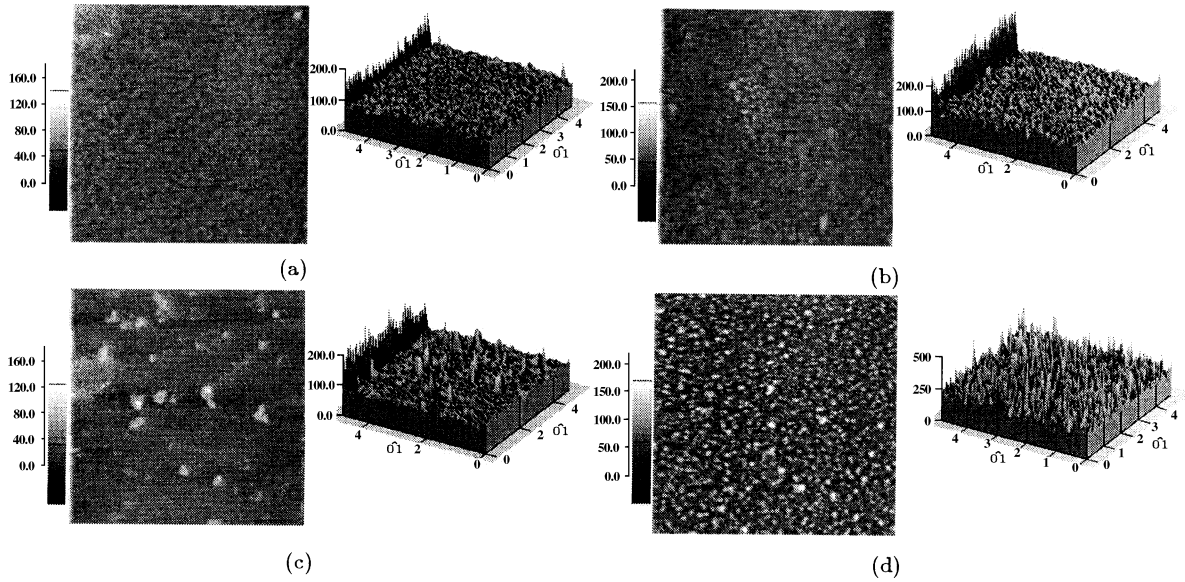


Fig.2. AFM micrograph of CZ-Si implanted with Er and annealed at various temperatures for 20s: a) as-implanted; b) 900°C; c) 1000°C; d) 1100°C.

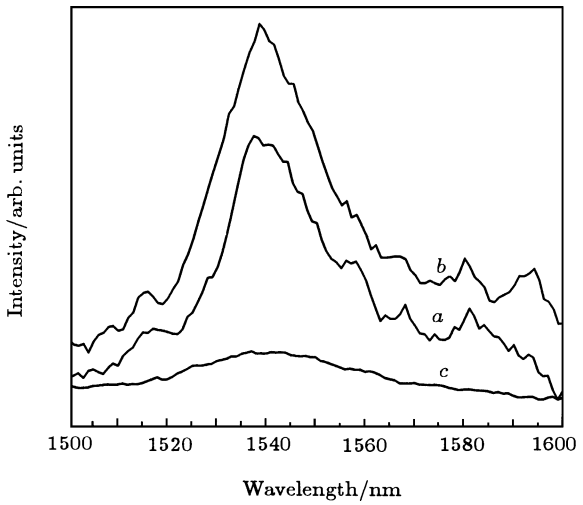


Fig.3. Near-infrared PL spectrum of Er-implanted CZ-Si at 77 K: curve *a*, 1×10^{16} Er/cm^2; curve *b*, 5×10^{16}Er/cm^2; curve *c*, 8×10^{16}Er/cm^2.

Figure 3 shows the near-infrared PL spectrum from the Si substrates implanted with different Er fluence after RTA at 1000°C for 20s, pumping the samples at 441.6 nm. The emission peak at 1536 nm is observed in 1×10^{16} Er/cm^2 implanted Si at 77K, which is due to the intra-4f transition of Er^{3+} from $^4I_{13/2}$ to $^4I_{15/2}$. The full width at half maximum (FWHM) is 22nm. With the Er fluence increasing to 5×10^{16}cm^{-2}, the PL intensity is a little larger than that from the 1×10^{16} Er/cm^2 implanted sample. The emission peak shifts to 1538nm and the FWHM broadens to 26nm. When the Er fluence reaches 8×10^{16}cm^{-2}, the PL intensity decreases by nearly one order of magnitude, and the FWHM enlarges greatly to 48nm. The luminescence quenches if the Er fluence continues to increase.

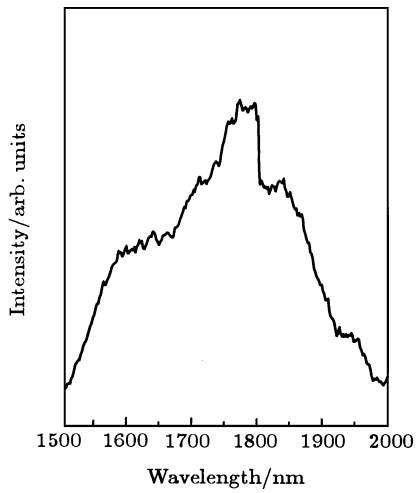


Fig.4. The as-implanted state near-infrared PL spectrum of 1×10^{16} Er/cm^2 implanted CZ-Si at 77K.

The luminescence from high-concentration Er-doped Si is due to the formation of nanometre needle Si on the surface of the implanted layer. Nonoptically active Er atoms may crystallize, and segregate and precipitate onto the surface. The Er concentration reaches the magnitude of 1×10^{21}cm^{-3}, most Er^{3+}, being in the implanted layer, may be excited to a higher energy level, and emit 1.54μm light through the recombination of electron-hole pairs produced in nc-Si (or c-Si). As the Er fluence increases, the self-annealing effect will enhance during ion implantation, and nc-Si may grow and react with Er resulting in nonoptically active Er silicide. Luminescence quench-

ing is inevitable. The increase of the FWHM is due to the thermal redistribution over the Stark levels. The Er ion fluence should be kept at lower than 5×10^{16}cm^2 and the ion flux should be smaller than 5μA·cm^{-2} in order to obtain 1.54μm light emission from Er-doped Si with MEVVA ion source.

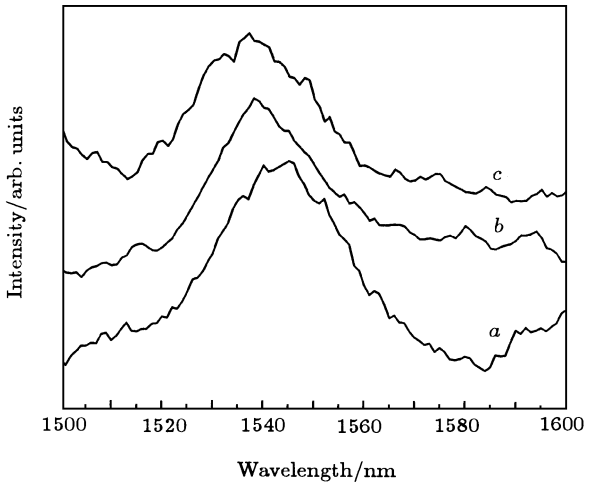


Fig.5. The 77 K near-infrared PL spectrum of 5×10^{16} Er/cm^2 implanted CZ-Si annealed at different temperatures: curve *a*, 900°C; curve *b*, 1000°C; curve *c*, 1100°C

No clear 1536 nm light signal can be detected at 77K in the as-implanted sample of 1×10^{16} Er/cm^2-implanted Si, as shown in Fig.4. This implies that Er^{3+} is nonoptically active before annealing, and the needle nc-Si structure has not come into being. A broad band of luminescence between 1500–2000 may originate from defects and damages induced by ion implantation. Figure 5 shows the PL spectrum for the Er-implanted silicon annealed at 900, 1000 and 1100°C for 20s. A broad emission peak around 1600nm excepting the sharp 1.54μm peak is detected, which implies that the defect elimination is incomplete after RTA at 900°C for 20s. In Fig.1 we can find that the high-density needle nc-Si structure has been formed on the surface after RTA. The spectra shape of Er^{3+} emission does not change appreciably for an annealing temperature from 900–1100°C. A relatively good Er PL intensity and FWHM from the sample annealed at 1000°C indicates that most defects are eliminated and disorder removed, which reduces the occurrence ratio of nonradiative transition through point defects or impurities at the same time. The formation of needle nc-Si significantly reduces the back-transfer strength because of its larger band gap than that of c-Si. If the annealing temperature and time continue to increase, it may help the growth of nc-Si and the recrystallization of Er, resulting in the reduction of the Er^{3+} PL yield. Above all, to attain optimum Er^{3+} light emission, it is necessary to anneal at about 1000°C for 20s.

Figure 6 shows the PL spectrum of Er-implanted CZ-Si at 10 K. The phonon-assisted near band edge emission of Si is centred around 1065nm in the as-implanted state. It should be noted that the minority carrier lifetime in the Si host is a crucial factor that determines the Er excitation efficiency. The increased Er luminescence intensity upon the additional 900–1100°C annealing is then attributed to a more efficient excitation due to the increased carrier lifetime. The Si PL intensity can be increased three-fold by subsequent thermal annealing at 1000°C for 20s. Annealing was also performed at other temperatures in the range of 500–1100°C, and it was found that annealing at 1000°C results in the optimum Er PL intensity at 1.54μm. Therefore, the additional 1000°C annealing increases the band edge emission, which is a signature of an increase in the minority carrier lifetime.

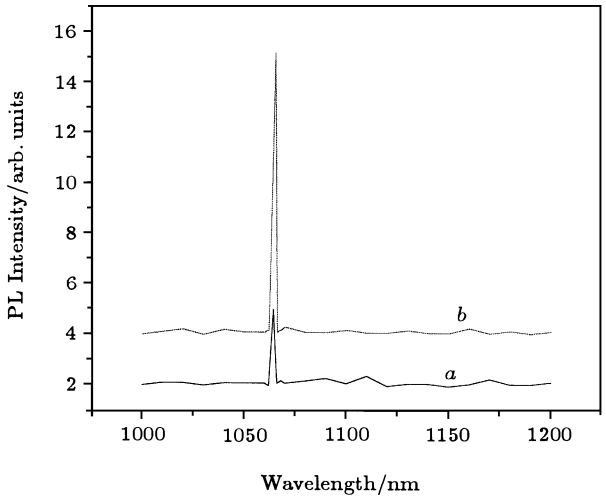


Fig.6. Phonon-assisted near band edge PL spectrum (measured at 10K) of 5×10^{16} Er/cm^2 implanted CZ-Si: curve *a*, as-implanted state; curve *b*, RTA at 1000°C for 20s.

IV. CONCLUSIONS

Er-doped silicon has been synthesized using a MEVVA ion source. The Er concentrations in the as-implanted sample were attained to ∼10at% corresponding to $\sim10^{21}$cm^{-3}. Needle nanometre crystalline silicon (nc-Si) was formed on the substrate surface. The crystallization, segregation and precipitation behaviours of Er in Er-doped silicon were closely related to ion implantation. The photocarrier mediated processes enabled energy transfer from nc-Si (or c-Si) to the Er^{3+} ions and resulted in light emission of 1.54μm.

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