Origin of Photoluminescence of Neodymium-Implanted Silicon*

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Abstract: Neodymium is incorporated into single crystalline silicon on MEVVA (Metal Vapor Vacuum Arc) ion source. At room temperature, strong ultra-violet and visible fluorescence are observed at the excitation wavelength of 220nm. Luminescence intensity increases with the increase of ion fluence. XPS results manifest that Si—O, Nd—O, Si—Si and O—O bonds exist in the implanted layers. Luminescence mainly results from the radiation transition in the intra-4f shell of Nd^{3+} ion. The defects' and damages' contribution to the luminescence is also presented.

Key words: photoluminescence; ion implantation; rare-earth

EEACC: 6170T; 6180J

CLC number: TN304.1+2 **Document code**: A **Article ID**: 0253-4177(2001)11-1377-05

1 Introduction

Silicon plays an important role in microelectronics, but its application in optoelectronics is limited because of its indirect energy gap. Many efforts have been made to develop Si-based light emitting materials with high light emission efficiency, which are essential in future optoelectronic integration. The discovery of porous silicon, which was integrated[1] for the first time, is great advancement in Si-based light emitting materials. The development of porous Si and nanometer science paves the way for nanometer light emitting materials[2]. In the meantime, new theory and technology make it possible to make progress in Si modification, impurity luminescence, defect engineering, and Si-based heteroepitaxy. The luminescent nanocrystal semiconductors embedded in SiO_2 are under investigation. Si-based embedded nanometer light emitting material is very important because of its great vitality and potential application in the opto-electronic integration[3—6]. As for rare-earth-doped materials, much attention has been paid to the erbium-doped silicon, because its characteristic emission at 1.54μm is occurring in the minimum absorption of optical fibers. Few reports can be found on neodymium-doped silicon, nevertheless, it is important to investigate the luminescence in Nd^{3+}-doped crystals[7,8] owing to the excitation of strongly quenched high-energy levels (the levels are 12,000cm^{-1} above the ground level $^4I_{9/2}$), because not only IR emission is produced from the $^4F_{3/2}$ level, but also UV and visible luminescence from upper levels, such as $^4D_{3/2}$.

This paper describes the luminescence in Nd ion implantation c-Si at the excitation wavelength of 220nm. XPS results manifest that there exist Si—O, Nd—O, Si—Si, and O—O bonds in the implanted layers. The mechanism of photolumi-

* Project Supported by National Natural Science Foundation of China Under Grant No. 59671051.

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Received 9 September 2000, revised manuscript received 3 April 2001

nescence has been discussed.

2 Experiment and Method

Czochralski (CZ)-grown n-type Si(111) was used in these experiments, with the resistivity of 3—4.5Ω·cm. The Si wafer was implanted on one side, with the average energy of the total Nd fluence of 1×10^{17}、4×10^{17} and $8\times10^{17}cm^{-2}$, about 100keV. The implantation was carried out on MEVVA (Metal Vapor Vacuum Arc) ion implanter at room temperature and the ion flux was 50 or $2.5\mu A/cm^{-2}$. Hitachi-F3010 ultra-violet fluorescence spectrometer with the resolution of 2nm was used to determine the PL spectrum of the samples at room temperature; the excitation wavelength was 220nm. XPS was performed on VG ESCALAB MKⅡ with the whole resolution of 0.2eV and the background pressure of 1×10^{-7}Pa. The X-ray source came from Mg-Kα.

3 Results and Discussion

Figure 1 shows the ultra-violet and visible photoluminescence of Nd ion incorporation single crystalline silicon without annealing. The PL spectra divides into two regions: one is in the wavelength between 350—600nm and the other in the wavelength between 700—800nm. The intensity of photoluminescence increases with the Nd ion fluence increasing, as implies that Nd ion plays an important role in the emission of light. In the sample of $8.0\times10^{17}cm^{-2}$ Nd ion incorporation c-Si, within the range of 350—600nm, there are distinct five emission bands centered around 400, 470, 507, 567 and 600nm, with the sharp peaks at 400 and 470nm, and wide emission bands center at 507, 567 and 600nm. Beside the emission peak at 400nm, two shoulder peaks can be observed. Within the range of 700—800nm, there are one clear luminescence band center around 724nm, and two shoulder peaks at 716 and 730nm.

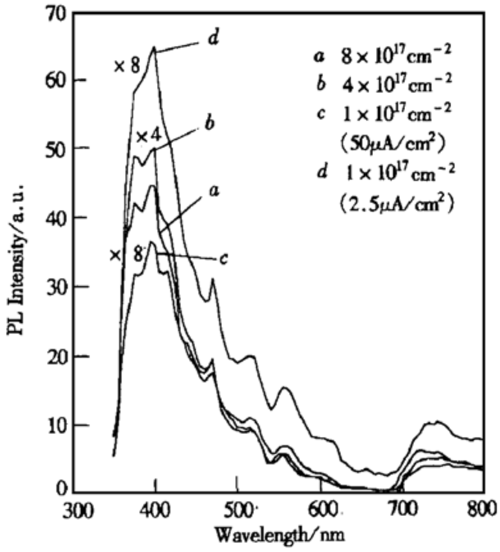

FIG. 1 Ultra-Violet and Visible Fluorescence Spectra of Neodymium Ion Implantation Single Crystalline Silicon Pumped at Wavelength of 220nm at Room Temperature The Sample of $1\times10^{17}cm^{-2}$ Nd was implanted with two kinds of ion flux, 2.5 and $50\mu A/cm^2$. Others were implanted with ion flux of $50\mu A/cm^2$, and the samples are as-implanted.

Similar PL spectrum can be found in other samples implanted with different ion fluence except the 400nm band, whose shoulder peaks are at 377 and 414nm. It should be noted that the luminescence intensity of the samples implanted with ion flux of $50\mu A/cm^2$ is lower than that of the sample implanted with ion flux of $2.5\mu A/cm^2$.

In rare-earth-doped materials, PL usually originates from the electron transition in intra-4f shell of rare-earth ions. There exhibit separated sharp emission peaks in PL spectra because the rare-earth ions are insensitive to the temperature and external environment. However, no such separated sharp emission peaks can be observed in the PL spectra of Nd ion incorporation c-Si. PL can also originate from the multiple emission centers. X-ray Photoelectron Spectra (XPS) can be used to investigate the chemical states and binding states. Figures 2 and 3 show that Si—O, Nd—O, Si—Si, and O—O bonds exist in the implanted layers. The standard binding energy of Si2p in c-Si and SiO_2 is 99.4 and 103.4eV, respectively. In Fig. 2, the binding energy

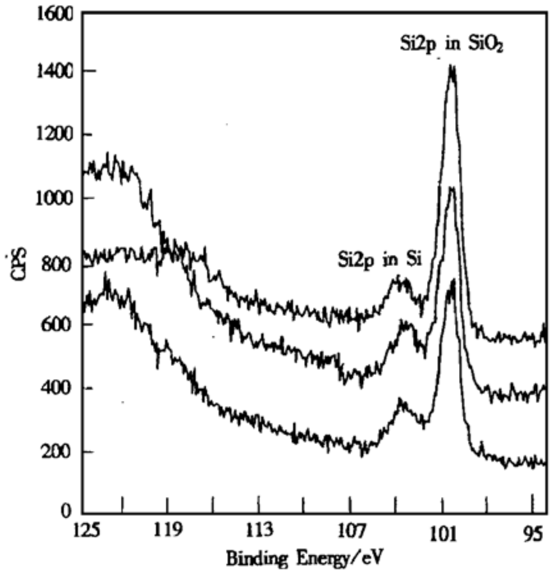

FIG. 2 XPS Spectra of Si2p in Nd-Implanted CZ-Si (100keV, As-Implanted) The spectra from top to bottom are for the samples with a total fluence of 1×10^{17}, 4×10^{17} and $8\times 10^{17}cm^{-2}$, respectively.

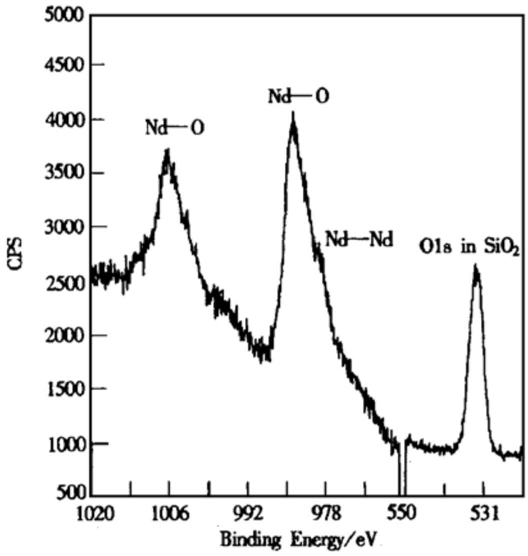

FIG. 3 XPS Spectra of Nd-implanted CZ-Si(4×10^{17} cm^{-2}, 100keV, As-Implanted) in Near Binding Energy of Nd3d and O1s

has a little deviation from the standard binding energy. Si2p is located at 100.1 and 103.6eV, respectively. Between them there are transitional peaks, maybe SiO_x, in the implanted layers. Oxygen is obtained from CZ-Si with an oxygen background concentration of $(1.7\pm 0.5)\times 10^{18}cm^{-3}$[9]. Moreover, during the ion implantation, Nd combining with oxygen may incorporate into silicon wafer because the rare-earth elements are rather active. Because XPS measurement is not in situ, O may incorporate into the implanted layer in the air. Nd—O bonds in Fig. 3 verifies the existence of oxygen. The bands of 470nm and 724nm may result from the neutral oxygen vacancy in SiO_2($O_3\equiv Si-Si\equiv O_3$)[10]; and the 600nm band is caused by some defects in SiO_2, whose microstructure is still unknown[11]. Electron transition in intra-4f shell of Nd^{3+} ion also contributes to the three luminescence bands. The blue emission band around 470nm and yellow emission band around 600nm correspond with $^4D_{3/2}\rightarrow {}^4I_{15/2}$ and $^2G_{7/2}\rightarrow {}^4I_{13/2}$, respectively; the red emission band around 724nm is associated with $^4F_{7/2}\rightarrow {}^4I_{9/2}$ ground state transition[12]. These three kinds of transition are shown in Fig. 4. Different luminescence centers are seen to be overlapped in the same region of light emitting. With the increase of Nd^{3+} ion flu-

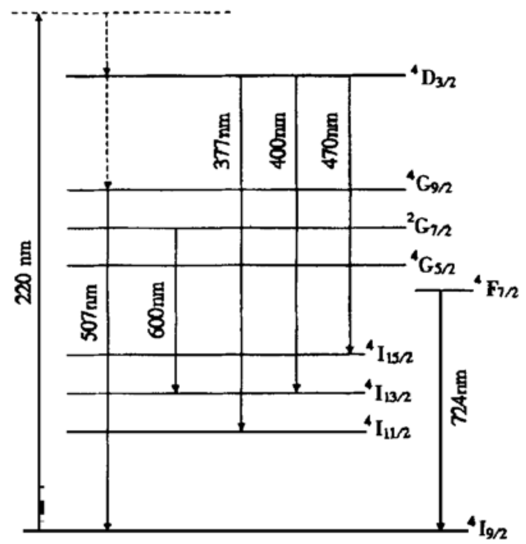

FIG. 4 Simplified Energy-Level Diagram of Nd^{3+} Ions Indicating PL Pumping, Relaxation Processes and Luminescence at Wavelength of 220nm Upward arrows indicate pump photons and downwards arrows stand for fluorescence emission. A broken vertical line represents a nonradiative transition, while a broken horizontal line represents a virtual state.

ence, Nd^{3+} ion concentration increases and enhances the effect of the oxygen vacancy, thereby increasing the PL intensity.

The 507nm band can be obtained through the electron recombination of $^4G_{9/2} \rightarrow {}^4I_{9/2}$; while the 567nm band is attributed to the oxygen enrichment near the Nd^{3+} ions center, which reduces the oxygen content in SiO_2 and form SiO_x. During the implantation at high ion fluence ($8.0 \times 10^{17} cm^{-2}$) and strong ion flux ($50\mu A/cm^2$), a large quantity of SiO_x particles are generated. It can seen from the XPS that SiO_2/Si is proportional to the Nd^{3+} ion fluence in Fig. 3. For the samples implanted with 1×10^{17}, 4×10^{17} and $8 \times 10^{17} Nd^{3+}/cm^2$, the proportion of SiO_2/Si is 36.8%, 51.0% and 51.2%, respectively. Dangling bonds (O—Si—O) come upon during the implantation, as attributes to the violet emission of 414nm band, which can be observed in the PL spectrum of Ⅰ-and Ⅱ-type silica glass[13]. The strongest violet emission of 400nm is rather complicated, which is due to the radiation recombination of $^4D_{3/2} \rightarrow {}^4I_{13/2}$ in Nd^{3+} ions. However, the recombination of electrons and holes at the interface between crystalline Si and amorphous SiO_2 can also result in the emission of 400nm band. It combines two kinds of luminescence centers. The shoulder peak at 377nm is obviously originated from $^4D_{3/2} \rightarrow {}^4I_{11/2}$.

During the implantation of high ion fluence ($(1—8) \times 10^{17} cm^{-2}$) on MEVVA ion implanter, the Nd ions with the average energy of 100keV are well-distributed on the disordered layer, with the thickness 30nm at the surface. Large ion beam current ($50\mu A/cm^2$) increases the target temperature to 400—450℃, thereby enhancing the diffusion of implanted Nd atoms and silicon atoms in the implanted layer[12,14]. Because rare-earth elements are more active to oxygen than silicon, and the oxygen is from the CZ-Si enriches near the Nd^{3+} ion center, lacking of oxygen will bring a large quantity SiO_x particles. Oxygen vacancy ($O_3 \equiv Si—Si \equiv O_3$) and Dangling bond (O—Si—O) comes into being during the implantation, too. All these are contributed to the light emission as well as the electron-hole recombination at the interfaces between crystalline Si and amorphous SiO_x, which are overlapped with the radiation transition of intra-4f shell in Nd^{3+} ion. Therefore, intensive light emitting with relatively large FWHM can be observed.

4 Conclusion

In the fluorescence spectrum of neodymium ion implantation single crystalline silicon with the average energy of 100keV to a total fluence of $(1—8) \times 10^{17} cm^{-2}$, strong ultra-violet and visible fluorescence spectroscopy is observed at the excitation wavelength of 220nm. XPS results manifest that Si—O, Nd—O, Si—Si, and O—O bonds exist in the implanted layers. Luminescence is related with the radiation transition in intra-4f shell of Nd^{3+} ion, and defects or damages in the network of Si—O complexes. Different emission centers overlapped in the same region of the PL spectrum can enhance the PL intensity. Moreover, the increase of the PL intensity depends on Nd^{3+} ion concentration.

References

[1] L. T. Canham, Appl. Phys. Lett., 1990, **57**: 1046.
[2] F. Buda, J. Kohanoff and M. Parrinello, Phys. Rev. Lett. 1992, **69**: 1272.
[3] T. Simizu-Iwayama, S. Nakao and K. Saitoh, Appl. Phys. Lett., 1994, **65**: 1814.
[4] P. Mutti. G. Ghisloti, S. Bertoni, L. Bonoldi, G. F. Cerofolni, L. Meda, E. Grilli and M. Guzzi, Appl. Phys. Lett., 1995, **66**: 851.
[5] T. Komoda, J. Kelly, F. Cristiano, A. Nejim, P. L. F. Hemment, K. P. Homewood, R. Gwilliam, J. E. Mynard and B. J. Sealy, Nucl. Instr. and Meth. Phys. Res. B, 1995, **96**: 387.
[6] L. S. Liao, X. M. Bao, X. Q. Zheng, N. S. Li and N. B. Min, Appl. Phys. Lett., 1996, **68**: 850.
[7] R. M. Macfarlane, F. Tong, A. J. Silversmith and W. Lenth, Appl. Phys. Lett., 1988, **52**: 1130.
[8] W. Lenth and R. M. Macfarlane, J. Lumin., 1990, **45**: 346.
[9] A. Polman, J. Appl. Phys., 1997, **82**: 1.
[10] J. Wan, C. Sheng, F. Lu, S. Yuan, D. W. Gong, L. S. Liao, Y. L. Fang, F. Lin and Xun Wang, J. Lumin., 1999, **80**: 369.
[11] Ryoichi Tohmon, Hiroyasu Mizuno, Yoshimichi Ohki *et al.*,

Phys. Rev. B, 1989, **39**: 1337.

[12] G. Cheng, Z. Xiao, J. Zhu, S. Xu and D. Ye, Nucl. Instr. and Meth. Phys. Res. B, 1998, **135**: 550.

[13] H. Z. Song and X. M. Bao, Phys. Rev. B, 1997, **55**: 6988.

[14] Zhisong Xiao, Guoan Cheng, Tonghe Zhang and Fei Xu, Surface and Coatings Technology, 2000, **128—129**: 461.

钕离子注入单晶硅光致发光的起源*

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摘要: Nd 离子注入到 (111) 单晶硅中形成钕掺杂层, 室温下, 紫外光 (220nm) 激发得到了钕掺杂层的蓝紫光的光致发光谱, 且发光强度随离子注入的剂量增大而增强. X 射线光电子能谱分析表明掺杂层存在 Si—O, Nd—O, Si—Si 和 O—O 键. 发光主要是由于 Nd^{3+} 的 4f 内层电子的辐射跃迁所致, 同时, 离子注入带来的缺陷和损伤也能发光.

关键词: 光致发光; 离子注入; 稀土

EEACC: 6170T; 6180J

中图分类号: TN304.1+2　　**文献标识码**: A　　**文章编号**: 0253-4177(2001)11-1377-05

* 国家自然科学基金资助项目(59671051).

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2000-09-09 收到, 2001-04-03 定稿