Chapter 1

Introduction

1.1 Silicon based optoelectric device

Crystalline silicon (c-Si) is the dominant material in microelectronics and is one of the best-studies materials. c-Si does not show efficient light emission at room temperature, because of its band structure with an indirect band gap of ~1.1 eV and a small exciton binding energy (~ 15 meV). Therefore, c-Si has not been a useful material for the manufacture of active optical devices. In silicon science and technology, the desire for the integration of optoelectronic devices with silicon microelectronics has led to the search for Si-based materials and structures that emit with high quantum efficiency. One promising approach to overcoming the indirect nature of optical transition in silicon is the relaxation of the k-selection rule due to the spatial confinement in low-dimensional Si nanostructures. In fact, efficient light emission has been observed from Si nanocrystals and chain-like Si polymers. Visible luminescence from Si nanostructures initiated remarkable studies on optical properties of Si nanostructures. [1-10] In low-dimensional semiconductor systems, three categories are usually considered: two-dimensional (2D) quantum wells, one-dimensional (1D) quantum wires, and zero-dimensional (0D) quantum dots. Optical responses of low-dimensional systems are sensitive to the dimensionality of system. With decreasing dimension of the system, the exciton binding energy increases. The geometrical restriction of the exciton would enhance the oscillator strength of optical transitions even in Si indirect-gap semiconductors. The Bohr radius of the exciton in bulk c-Si is about 4 nm. For the observation of the size dependence of optical responses in Si materials, Si low-dimensional materials of a few nanometers size should be prepared.

Since the discovery of efficient visible photoluminescence (PL) from Si [11], Ge [12] and SiC [13] nanocrystals, there have been numerous reports describing visible luminescence properties of nanocrystals made from indirect-gap-IV semiconductors. In particular, efficient visible luminescence from porous Si [14] initiated remarkable theoretical and experimental studies on low-dimensional Si materials, because the PL efficiency or porous Si is very high and large porous layer is produced on c-Si wafer. In semiconductor nanostructures, low-dimensionality plays an essential role in optical transitions. Theoretical studies show the widening of the band-gap energy with decreasing size of 2D wells, 1D wires or 0D dots. A drastic size reduction to a few nanometers is need for the observation of strong visible light emission. Silicon photonic components are based on the optical properties of crystal silicon or crystalline Group IV alloys. Recent work has shown that infrared light (wavelength > 1.2 μm) can be waveguided, detected, emitted, modulated, and switched in silicon. Some physical properties of Si, such as indirect bandgap and low carrier mobility, pose obstacles to the realization of successful photonic devices.

There is a lot of interest to the electroluminescence (EL) of SiO_x-based light emitting diodes (LED) and lasers, as well as in optoelectronics-microelectronics integration using the current Si technology. Obtaining an efficient EL based on the material of nc-Si embedded oxide is a very important step toward the development of Si-based optoelectronics. The two tightly interconnected key issues that need to be solved are the understanding of the emission mechanism, and the fabrication technology. The first studies of EL properties of the SiO_x-based systems served as an additional tool for the investigation of the physical properties. EL of metal-SiO-Au thin film structures had been studied in connection with the bitable switching, negative resistance, and memory properties that silicon monoxide films exhibit. The workers of Di Maria *et al.* on the EL of SiO_x-based system originated from the investigations of the films that are important in the microelectronics industry, such as thermal- and chemical vapor deposition (CVD)-silicon-reach oxide films [15]. The SiO_2 film has been used as a typical insulting layer in most Si based device. However, for the oxygen terminated Si/SiO_2 structure, the oxygen modified interface states play predominant role in the properties of light emission. At the Si nanocrystal (nc-Si)/SiO_2 interfaces, there are also radiative interface states located in the band gap of nc-Si. This three-energy-level system may play an essential role in population inversion and optical gain process under strong excitation, which is very important for the applications in the bright Si LED and Si laser.

1.2 Background of nanocrystallite Si

The quantum confinement effect in silicon structures of nano-metric size constitutes an approach to engineering a direct transition and the emission of visible light. The larger band gap with respect to bulk Si arises as a consequence of fundamental quantum mechanics where energy levels for a particle inside a potential box will be moved in energy depending on the box size. Valence state will be shifted down and conduction states will be shifted up in energy, so that the effective bandgap will be enlarged.

Confinement in a small size has other effects on the recombination mechanisms [16]: carriers become localized and cannot diffuse to defects and thus Shockley-Read-Hall recombination is suppressed. Auger recombination is also absent until two excitons are created within the same nanocrystals. Moreover, reducing the size radiative recombination becomes more efficient since electron and hole wavefunctions overlap more and more in space causing faster recombination.

In 1990 Canham demonstrated that Si nanostructures may be useful for optoelectronics due to room temperature enhanced emission of light with respect to bulk Si for porous silicon [17, 18]. The reason of this is attributed to the low dimensionality of the surviving Si skeleton. After the discovery of bright PL in porous silicon, research on light emission from Si nanostructure has been very impressive.

Nc-Sis embedded in SiO_2 films are widely studied because the intense visible and near-IR PL at room temperature is observed from such nanocomposite systems. The SiO_2 matrix is a well confiner to offer a high bandgap structure confining the smaller bandgap of silicon. Moreover, the light amplification in nc-Sis embedded in SiO_2 matrix has been demonstrated [19]. However, the behavior of light emission from Si/SiO_2 interface is more complicated and still unclear. The defects or oxygen-deficiency centers also play important roles to control the luminescence of the SiO_x film. Nanocrystallite Si structures that exhibit quantum confinement effect have led to the development of novel Si-based functional devices such as light emitting diodes, resonant tunneling diode and single-electron transistor, etc. [11-13] In particular, most investigations on preparing silicon oxide or nitride with buried Si nanocrystals (nc-Si) in matrices have been performed using plasma-enhanced chemical vapor deposition (PECVD), in which pure monosilane (SiH_4) and nitrous oxide (N_2O) or ammonia (NH_3) are decomposed at high plasma power from 100 to 450 W. [14, 20] The PECVD deposition associated with subsequent heat treatment enables the easy deposition of a Si-rich SiO_x film with a sufficiently high density of excess Si atoms by controlling the fluence of reactive gases.

Silicon-rich SiO_2 (SiO_x) materials can be synthesized by electron-beam evaporation [21], RF-magnetron sputtering, Si-ion-implantation [22] and plasma-enhanced chemical vapor deposition (PECVD) [23], etc. Si-ion-implantation has recently emerged as an alternative method of synthesizing

Si nanocrystals (nc-Si) in SiO_2 matrix. Previously, porous Si [24], PECVD-grown Si-rich SiO_2, amorphous Si:H:O, and Si-implanted SiO_2 (SiO_2:Si^+) have been shown to exhibit PL and EL spreading from blue-green to near infrared region (340-800 nm) region [1, 25-29]. Various defect-related blue-green PL [30-34] bands from SiO_2:Si^+ materials have been identified to originate from principle defects such as the neutral oxygen vacancy (NOV, denoted as $O_3\equiv Si–Si\equiv O_3$) with PL at 410-460 nm [35], and the precursor of nc-Si (E'_δ, denoted as Si$\uparrow$Si–Si) with PL at 520-550 nm [36], the non-bridging oxygen hole center (NBOHC) [35, 36], among others. Some of irradiative defects such as NOV and NBOHC can be activated via appropriate annealing processes. The contribution of NOV defects to the PL at 450-470 nm has been verified in previous reports [19-21], whereas the nanocrystallite Si (nc-Si) embedded in the annealed SiO_2:Si^+ matrix contributes to the emission at longer wavelengths [11]. The high-temperature annealing of SiO_2:Si^+ usually quenches defects and causes the generation of nc-Si, providing a more pronounced near-infrared PL (700-900 nm). The nc-Si related PL wavelength depends strongly on the size of nc-Si. Identifying these irradiative defects in SiO_2:Si^+ film is very important for white-light emitting applications. The Si-rich SiO_2:Si^+ material with self-assembled Si quantum dots has attracted considerable interest for their potential use in fabricating novel light-emitting or charge-storage devices. Although two contradictory PL mechanisms exist, most studies focus on the nc-Si-correlated PL characteristics, while few studies have investigated the defect-induced blue-green PL.

1.3 Motivation of Si nanocrystal based light emitting diode (LED)

Several types of SiO_x films and SiO_x-film-based systems are being investigated in order to obtain high efficient LED. However, the stability of most nanocrystallized silicon-based LED is poor. Since PECVD-grown SiO_x film has been considered as a good material to precipitate nc-Si, this process can easily deposit great amount of excess silicon and precipitate more nc-Si after high temperature annealing. It even reported that the gain was found in the PECVD-grown SiO_x film after high temperature annealing [4]. Therefore, understanding optimum manufacturing-process for the highest luminescence from nc-Si buried in SiO_2, moreover, knowing the role of nc-Si in SiO_2, and illustrating the mechanism of photoluminescence and electroluminescence are the most interesting issues. Finally, to realize an nc-Si-buried MOSLED and even the LED with nano-pyramid and nano-pillar structures are also achieved. PECVD grown Si-rich SiO_2 or SiO_x with embedded Si nanocrystals of extremely high density have been extensively investigated as a new class of light emitting material over decades [11-16]. To obtain room temperature EL, both the metal/SiO_x/Si and the metal/PECVD-grown SiO_x/p-Si based LEDs were demonstrated [17, 18], in which Fowler-Nordheim (F-N) and direct p-n junction barrier tunneling mechanisms were known to play important roles for the light emission from Si nanocrystals. However, the EL responses of such devices are usually not efficient due to the requirement of extremely high electric field for carriers tunneling through the insulating oxide channel [19, 23]. Therefore, versatile solutions have recently been developed to enhance the carrier injection efficiency, such as changing the contact metals, shrinking the optical bandgap, decreasing the barrier height, and reducing the resistivity of the host material, etc.

1.4 Organization of dissertation

The work described in this dissertation concentrates on the derivation of the electro- and photo- luminescence from the Si nanocrystal based metal oxide semiconductor diode, the diagnosis of the Si-rich SiO_2 matrices with buried Si nanocrystal, and the quantum efficiency improvement of the Si nanocrystal based metal oxide semiconductor light emitting diode.

This dissertation is organized as follows: Chapter 2 derives the optical and electrical characteristics of a metal-oxide-semiconductor diode on SiO_2/Si by multi-recipe Si-ion-implantation. First, we will fabricate Si-rich SiO_2 matrix by the Si-ion-implantation approach and precipitate luminescent centers by high temperature annealing process. Furthermore, by the luminescent measurement, we can derive what kind of the luminescent center in Si-implanted SiO_2, the evolution of luminescent center in Si-implanted SiO_2 and the roles of Si-based defects or Si nanocrystals in Si-implanted SiO_2 matrix. Chapter 3 derives the optical and electrical characteristics of a plasma enhanced chemical vapor deposition (PECVD) grown metal-oxide-semiconductor diode with buried Si nanocrystal. First, we analyze the luminescent efficiency of the PECVD-grown Si-rich SiO_2 film deposited at a high-plasma power under low substrate temperature and a low-plasma power under high substrate temperature. That is, we demonstrate the optimum process conditions to obtain the Si-rich SiO_2 matrix with the largest density of excess Si atoms. In order to locally precipitate Si nanocrystal, we further demonstrate CO_2 laser annealing process to overcome the high-temperature destruction for the nearby electric integrated circuit. The carrier transport mechanism in the metal oxide semiconductor diode is also discussed. In Chapter 4, we study and demonstrate the electrical and optical improvements of the Si nanocrystal based light emitting diode with the interfacial Si nano-pyramid structure between the SiO_2 and Si substrate. We also derive the high external quantum efficiency of the Si nanocrystal based light emitting diode with the Si nano-pillar structure. Finally, Chapter 5 summarizes the dissertation and gives some future directions.

References

[1] D. J. DiMaria, J. R. Kirtley, E. J. Pakulis, D. W. Dong, T. S. Kuan, F. L. Pesavento, T. N. Theis, and J. A. Cutro, J. Appl. Phys. **56**, 401 (1984).

[2] G. G. Qin, Y. Q. Wang, Y. P. Qiao, B. R. Zhang, Z. C. Ma, and W. H. Zong, Appl. Phys. Lett. **74**, 2182 (1999).

[3] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo, and F. Priolo, Nature **408**, 440 (2000).

[4] A. Irrera, D. Pacifici, M. Miritello, G. Franzò , and F. Priolo, F. Iacona, D. Sanfilippo, G. Di Stefano, and P. G. Fallica, Appl. Phys. Lett. **81**, 1866 (2002).

[5] G.-R. Lin, C. J. Lin, C. K. Lin, L. J. Chou, and Y. L. Chueh, J. Appl. Phys. **97**, 094306 (2005).

[6] L.-Y. Chen, W.-H. Chen, and F. C.-N. Hong, Appl. Phys. Lett. **86**, 193506 (2005).

[7] M. Perálvarez, C. García, M. López, B. Garrido, J. Barreto, C. Domínguez, and J. A. Rodríguez, Appl. Phys. Lett. **89**, 051112 (2006).

[8] C. Huh, N.-M. Park, J.-H. Shin, K.-H. Kim, T.-Y. Kim, K. S. Cho, and G. Y. Sung, Appl. Phys. Lett. **88**, 131913 (2006).

[9] R. Huang, K. J Chen, P. G. Han, H. P. Dong, X. Wang, D. Y. Chen, W. Li, J. Xu, Z. Y. Ma, and X. F. Huang, Appl. Phys. Lett. **90**, 093515 (2007).

[10] G.-R. Lin, C. J. Lin, H. C. Kuo, H. S. Lin, and C. C. Kao, Appl. Phys. Lett. **90**, 143102 (2007).

[11] H. Takagi, H. Ogawa, Y. Yamazaki, and A. Ishizaki, Appl. Phys. Lett. **56**, 2379 (1990).

[12] Y. Maeda, N. Tsukamoto, and Y. Yazawa, Appl. Phys. Lett. **59**, 3168 (1991).

[13] T. Matsumoto, J. Takahashi, T. Tamaki, T. Futagi, and H. Mimura, Appl. Phys.

Lett. **64**, 226 (1994).

[14] Q. Ye, R. Tsu, and E. H. Nicollian, Phys. Rev. B **44**, 1806 (1991).

[15] A. Pèrez-Rodrìguez, O. González-Varona, B. Garrido, P. Pellegrino, J. R. Morante, C. Bonafos, M. Carrada, and A. Claverie, J. Appl. Phys. **94**, 254 (2003).

[16] D. Pacifici, E. C. Moreira, G. Franzo, V. Martorino, and F. Priolo, Phys. Rev. B **65**, 1441091-1 (2002).

[17] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[18] X. Zhao, O. Schoenfeld, J. Kusano, Y. Aoyagi, and T. Sugano, Jpn. J. Appl. Phys. **33**, L899 (1994).

[19] P. Mutti, G. Ghislotti, S. Bertoni, L. Bonoldi, G. F. Cerofolini, L. Meda, E. Grilli, and M. Guzzi, Appl. Phys. Lett. **66**, 851 (1995).

[20] T. Shimizu-Iwayama, K. Fujita, S. Nakao, K. Saitoh, T. Fujita, and N. Itoh, J. Appl. Phys. **75**, 7779 (1994).

[21] H. Takagi, H. Owada, Y. Yamazaki, A. Ishizaki, and T. Nakagiri, Appl. Phys. Lett. **56**, 2379 (1990).

[22] S. Tong, X. N. Liu, T. Gao, and X. M. Bao, Appl. Phys. Lett. **71**, 698 (1997).

[23] L. S. Liao, X. M. Bao, X. Q. Zheng, N. S. Li, and N. B. Min, Appl. Phys. Lett. **68**, 850 (1996).

[24] H. Z. Song, X. M. Bao, N. S. Li, and J. Y. Zhang, J. Appl. Phys. **82**, 4028 (1997).

[25] G. G. Qin, A. P. Li, B. R. Zhang, and B. C. Li, J. Appl. Phys. **78**, 2006 (1995).

[26] H. Z. Song and X. M. Bao, Phys. Rev. B **55**, 6988 (1997).

[27] W. Hayes, M. J. Kane, O. Salminen, R. L. Wood, and S. P. Doherty, J. Phys. C **17**, 2943 (1984).

[28] H. Nishikawa, E. Watanabe, D. Ito, M. Takiyama, A. Leki, and Y. Ohki, J. Appl. Phys. **78**, 842 (1995).

[29] R. Tohmon, Y. Shimogaichi, H. Mizuno, Y. Ohki, K. Nagasawa, and Y. Hama, Phys. Rev. Lett. **62**, 1388 (1989).

[30] K. Vanheusden and A. Stesmans, J. Appl. Phys. **74**, 275 (1993).

[31] Y. Sakurai and K. Nagasawa, J. Appl. Phys. **86**, 1377 (1999).

[32] H. Nishikawa, E. Watanabe, D. Ito, Y. Sakurai, K. Nagasawa, and Y. Ohki, J. Appl. Phys. **80**, 3513 (1996).

[33] M. Ya. Valakh, V. A. Yukhimchuk, V. Ya. Bratus, A. A. Konchits, P. L. F. Hemment, and T. Komoda, J. Appl. Phys. **85**, 168 (1999).

[34] H. Nishikawa, R. E. Stahlbush, and J. H. Stathis, Phys. Rev. B **60**, 15910 (1999).

[35] J. C. Cheang-Wong, A. Oliver, J. Roiz, J. M. Hernandez, L. Rodrigues-Fernandez, J. G. Morales, and A. Crespo-Sosa, Nucl. Instr. And Meth. in Phys. Res. B **175-177**, 490 (2001).

[36] H. S. Bae, T. G. Kim, C. N. Whang, S. Im, J, S. Yun, and J. H. Song, J. Appl. Phys. **91**, 4078 (2002).