Research on Optical Properties of Porous Materials Activated by Luminescence Centers

发光离子掺杂多孔材料光学特性的研究

萨初荣贵 著

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Chapter 1 Introduction

1.1 Porous materials

1.1.1 Porous silicon thin films

1.1.1.1 Why porous silicon thin film

Porous silicon (Si) is a three dimensional network of Si nanocrystals, which is first discovered by Uhlir in 1956[1]. Since porous Si is compatible with Si processes, it is known to be the most important material in Si based photonics. Since the discovery of multicolor room temperature emission from nanoporous Si, porous Si has further evoked intense interest[2-4]. The emission wavelength can be extended to the near infrared region by thermal oxidation. However, the emission hardly covers the optical telecommunication wavelengths (from 1.0 μm to 1.6 μm)[5]. In general, luminescence center doping is an effective way to extend the application in communication technology. Porous Si is a very suitable host material for luminescence center doping because it consists of many open pores, and has large surface area. Luminescence centers can be doped very easily during or after the growth of porous Si. Another important advantage of porous Si as a host is ability to sensitize luminescence centers.

On the other hand, thin film integrated optics are becoming more and more important in optical communication technology. The technology for the fabrication of passive devices such as planar optical waveguides is well developed[6]. One next step is the development of waveguide optical amplifiers that can be integrated in passive devices. Since the refractive index of porous Si can be changed over a wide range by

controlling the porosity, waveguide interconnection can be produced by porous Si. Recently, rare earth ions doped porous Si has attracted great interest as a candidate material for waveguide optical amplifier[7-8]. For example, Er^{3+} doped porous Si shows emission at 1530 nm, the wavelength coincides well with the low loss window of silica based optical fibers. However, with the rapid development of the optical fiber communication networks in recent years, broader gain bandwidth in the telecommunication window is required. Very recently, Fujimoto and Nakatsuka[9] reported a novel infrared luminescence from bismuth (Bi) doped silica-based glasses ranging from 1.0 μm to 1.6 μm. Since the report of optical amplification in Bi doped silica glass, Bi doped various materials have been intensively studied[10-16]. In first part of this work, we focus on porous Si as a host material to study the optical properties of Bi-doped oxidized porous Si thin films for developing a broadband optical amplifier at the telecommunication wavelengths. This part summarizes the optical properties of porous Si based on the past reports, and then elucidates the purpose of this work.

1.1.1.2 Preparation of porous silicon

Generally, porous Si is prepared by electrochemical anodization (electrochemical etching) of bulk Si wafers in a solution of aqueous or ethanoic hydrofluoric acid (HF). Schematic diagram of porous Si formation set up was shown in Figure 1.1. By contacting the anodizing electrolyte, the porous Si is only formed on the surface of Si wafer. During the past years, several mechanisms for pore formation in Si substrate have been proposed[17-18]. Figure 1.2 shows a proposed porous Si formation mechanism by Lehmann and Gösele[18]. During the anodization process, the positively charged Si surface is oxidized by F^- ions followed by the formation SiF_6^{2-} and $2H^+$ complex. After the anodization, ethanol is added to remove the H_2 bubbles from the sample surface. Various kinds of porous Si can be simply prepared by controlling the preparation conditions, such as type of Si wafer, HF concentration and the acidity (pH value) in anodization solution, the anodization current density and anodization time, and so on[19-22].

1.1.1.3 Morphology of porous silicon

During the past years, the microstructure of porous Si has been widely studied

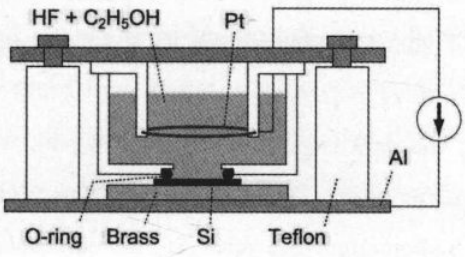

Figure 1.1 Anodization cell used for the fabrication of porous Si thin film

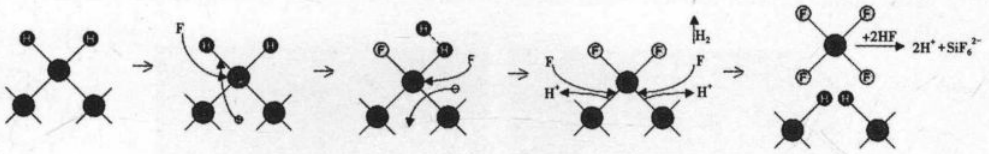

Figure 1.2 Suggested mechanism for the electrochemical dissolution of Si[18]

by many groups by means of microscopy techniques[19-24]. The pore type, pore size, porosity and porous thickness are known to be the main structural parameters of the porous Si. Based on the size of pores in porous Si, porous Si can be divided into three categories: microporous (less than 2 nm), mesoporous (between 2 to 50 nm), and macroporous (larger than 50 nm). To study the structure of porous Si, field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) measurements etc are commonly used. As shown in Figure 1.3, detailed information about pore size and morphology can be seen from the cross-sectional SEM image[25].

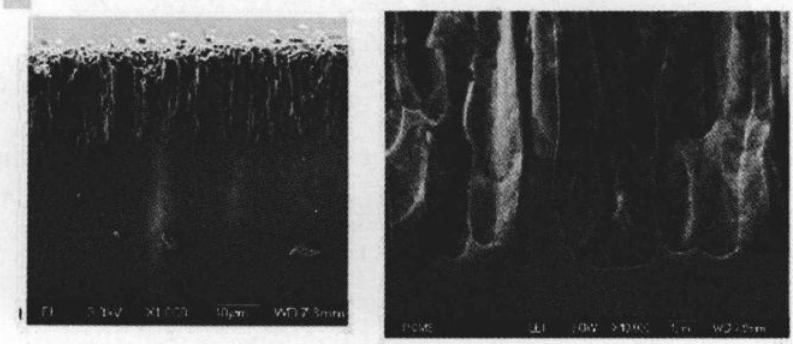

Figure 1.3 Cross sectional SEM image of porous Si[25]

Furthermore, the surface structure of oxidized porous Si was observed by TEM in our group[26]. Figure 1.4 shows (a) plain-view TEM images of as-prepared porous Si and plain-view TEM images of porous Si oxidized at (b) 800 ℃, (c) 900 ℃, (d) 1000 ℃. In Figure 1.4, the dark regions correspond to porous Si skeletons, while the bright regions correspond to pores. We can see that the pore size (diameter of the pores) is several tens of nanometers. The pore size decreases with increasing annealing temperatures. When annealed at the highest temperature, that is, 1000 ℃, although pores still remain, the size is much smaller than that in the as-prepared sample.

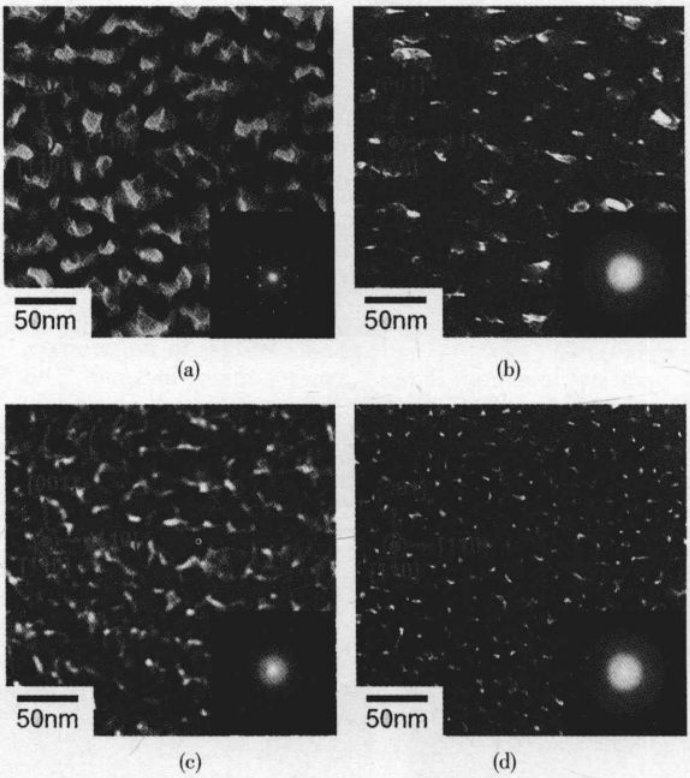

Figure 1.4 (a) Cross-sectional and (b) plain-view TEM images of as-prepared porous Si and plain-view TEM images of porous Si oxidized at (c) 900 ℃ and (d) 1000 ℃[26]

1.1.1.4 Luminescence of porous silicon

Since the first report on the room temperature luminescence in the visible range by L. T. Canham in 1990, porous Si has evoked much interest[27]. After then, further study on the luminescence properties by the group indicated that porous Si contains

quantum size crystalline structures responsible for the visible emission[28]. Recently, luminescence properties of porous Si are widely investigated. Usually, porous Si is terminated with Si-H bonds. Due to the weak bonding in the hydrogen termination, non-radiative defect centers can be formed under light illumination, making porous Si not so stable. One way to solve the problem is thermal oxidation or electrochemical oxidation[5, 29-30].

Porous Si shows near infrared (NIR) luminescence after thermal treatment. Photoluminescence (PL) properties of porous Si at the oxidation temperature from 0 ℃ to 1200 ℃ were investigated by Nakamura et al[5]. It was found that NIR luminescence can be observed in the high temperature annealed oxidized porous Si. As shown in Figure 1.5, the peak position and intensity of the oxidized porous Si strongly depend on the oxidation temperature. Visible luminescence is observed in the as prepared sample and the samples annealed at low temperature. The PL intensity in the NIR region is steeply quenched after annealing at 300 ℃, and recovered at above 700 ℃. XPS measurement suggests that the formation of thick high-quality SiO_2 layer under high temperature annealing results in the PL intensity recovery. It is concluded that the thickness and quality of SiO_2 layer play a crucial role in the PL properties of the thermally oxidized porous Si.

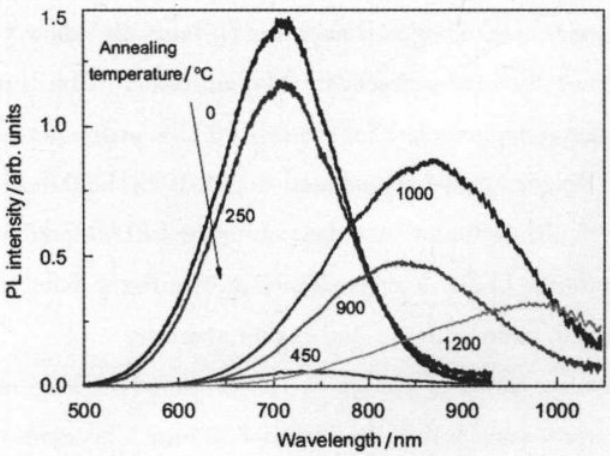

Figure 1.5 PL spectra of the porous Si powders oxidized from 0 ℃ to 1200 ℃[5]

1.1.1.5 Applications of porous silicon

Various excellent characteristics of porous Si have given rise to a variety of potential applications, such as Si-on-insulator(SOI), light emitting diodes(LEDs), waveguide and so on. A full wafer SOI structure based on porous Si can be easily formed. For example, a porous Si layer is prepared in a Si wafer and thereafter is anodically oxidized in the same cell for the preparation of the porous layer using an oxidant electrolyte solution without HF. The anodic oxidation can lead to the formation of an oxide layer located only at the bottom of the porous layer, the result being a structure porous Si/ anodic oxide/Si substrate. A following high temperature annealing can densify the anodic oxide and introduce re-crystallization of the remaining porous Si layer. The process lead to an SOI structure[31-33]. During the 1980's, many research on porous Si were carried out to develop SOI technology for device isolation in integrated circuits. A method is based on the oxidized porous Si to isolate pre-defined islands of crystalline Si from the bulk Si substrate. Compared to conventional methods, the full isolation by oxidized porous Si method offered the advantages of higher speed, lower power consumption, higher packing density and a reduced number of fabrication steps[34]. Another advantage is the simplicity of processing and low leakage current[35].

LEDs based on Si would find many applications, such as very large scale integration and display technology. However, Si normally shows only very weak infrared luminescence. Since the discovery of multicolor visible luminescence from porous Si, it has generated much interest. In 1990's many porous Si LEDs were proposed[36-38]. L. Pavesi et al demonstrated a porous Si LED based on a resonant planar microcavity[36]. They found that the porous Si LED offered a few advantages compare to conventional LED: higher efficiency, narrower band emission, higher directionality of the emission pattern, and higher stability.

Since the refractive index of porous Si can be tuned in wide range, by varying the porosity, it is worth considering the material to form waveguide interconnects. In 1995, optical waveguiding has been observed in oxidized porous Si on SiO_2 isolating layer on Si substrate. The schematic view of the optical waveguide based on oxidized porous Si is shown in Figure 1.6[39]. Since then, many approaches to manufacture

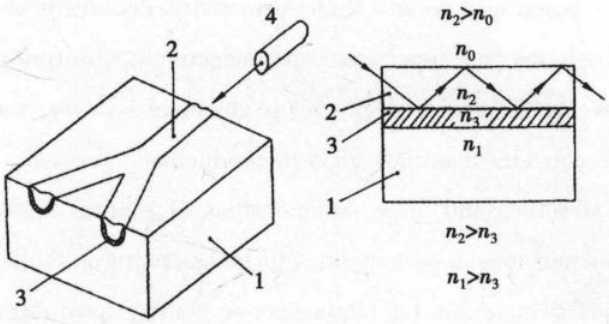

Figure 1.6 Schematic view of optical waveguide based on oxidized porous Si[39]

1—Si substrate; 2—oxidized porous Si; 3—Si oxide layer; 4—light source

active porous Si layers based waveguides operating from visible to infrared wavelengths have been demonstrated[39-42]. In Ref. [42] it was found that it is possible to produce integrated optical waveguides based on oxidized porous Si. The fabrication process is compatible with the traditional Si technology and consists of the formation of local layers of porous Si followed by thermal oxidation of the layers. Active waveguide devices in telecommunication wavelengths can be obtained by introducing luminescence centers into the waveguide channel. Er^{3+} is of special interest for this purpose, since its main emission band with peak wavelength at 1530 nm corresponds to minimum loss of the quartz fiber[40, 41, 43]. Recently, Er^{3+} doped oxidized porous Si waveguides were extensively investigated, an optical losses and internal gain in Er doped porous Si waveguide reached 2dB/cm and 5.8 dB/cm at a pumping power of 65 mW, respectively[40]. The gain is much larger than that in Er^{3+} doped Si rich silica waveguide (0.58 dB/cm) at low power pumping[44]. In first part of this work, the broadband NIR luminescence from Bi doped oxidized porous Si thin film is studied, aiming for its potential application in broadband optical waveguide amplifier at optical telecommunication wavelengths.

1.1.2 Zeolites

1.1.2.1 Why zeolite

Zeolite is a highly crystalline porous material, which has many excellent features, such as microporous uniformity, structural symmetry, and topological variety. These properties result in high surface areas, thermal stability, and the ability

to sieve molecules based on size and shape-selectivity. Zeolites have been widely used in applications such as gas separation and selectively absorption, ion exchange, catalysis, and have been suggested for use as chemical sensors, membrane reactors, and low dielectric constant materials for semiconductors.

The porous structure and large surface areas of zeolites enable them to act as hosts for molecules and ions or as templates for nanostructures synthesis[45]. Recently, zeolites acting as host materials for luminescence centers have attracted considerable attention for constructing functional materials designed at nanosized levels. Luminescence centers[rare earth(RE) ions, Bi, and so on] can be simply doped in zeolite by a simple ion exchanging. Optically activated zeolites show various potential applications, such as fiber amplifiers, LEDs, biological probes, lighting, laser materials, and so on[46-49]. In addition, zeolite is one of the most suitable host materials for the formation of metal clusters. Metal clusters are known to be chemically stable in the nano-sized pores in the cage, and can be formed by a simple ion exchange process followed by a thermal treatment. In second part of this work, photosensitization of RE ions by silver clusters/ions in zeolites is studied. This part summarizes the optical properties of zeolite based on past reports, and then elucidates the purpose of this work.

1.1.2.2 Structure

Zeolites arealuminoslilicate crystalline nanoporous material with small pores(1 - 2 nm diameter). The aluminosilicate framework consists of corner sharing orthosilicate (SiO_4) and orthoaluminate (AlO_4) tetrahedra units by sharing oxygen between every two consecutive units, and cations located inside channels or cavities to balance negative charges in the framework[50]. Zeolite is defined as crystalline structure due to its regular porous shape and size. Zeolites can be prepared with a wide range of shapes and pores size, and the composition can be modified during preparation, in order to tailor the properties. Zeolites also can be prepared with various silica to alumina ratios, but the constraints are that the sum of the number of Si atoms and the number of Al atoms equals 192 and that the total charge of the cations equals the number of Al atoms[51-52].

As shown in Figure 1.7, the sodalite cage(or β cage) is known to be the basic

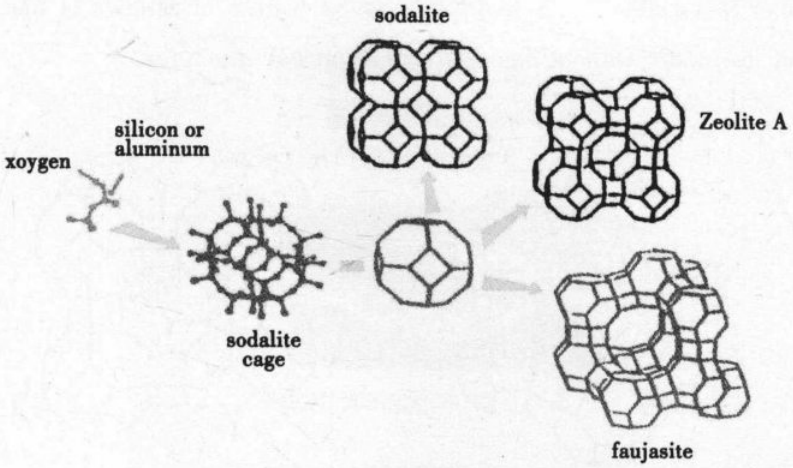

Figure 1.7 Basic building block of zeolite[53]

building block of zeolites[53]. The sodalite cage has both four-membered and six-membered rings in its structure. By fusing together the four-membered rings, sodalite is formed and which is a naturally occurring material. By bridging the four-membered rings, zeolite A is formed. This does not occur in nature, but is industrially produced on a massive scale. If the six-membered rings are bridged(prism), then possibly the most important zeolite structure, zeolite X and Y [faujasite (FAU) type zeoltie] is formed. The X and Y are divided by the ratio of silicon/aluminum. This structure has very large microporous spaces, allowing organic molecules to diffuse in and out. Another important class is the pentasil zeolites, named so because they are constructed of five-membered rings. The most important example is that of ZSM-5. FAU type zeoltie is one of the most widely used zeolite [Figure 1.8(a)]. The diameter of the entrance to the supercage is about 0.75 nm, whereas the diameter of the supercage itself is about 1.2 nm. In contrast, the diameter of the sodalite cage is 0.66 nm and that of the hexagonal prism is 0.18 nm. On the other hand, zeolite A exhibits the LTA(Linde Type A) structure[Figure 1.8(b)]. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes. The pore diameter is defined by an eight member oxygen ring and is small at 0.42 nm. This leads to a larger cavity of minimum free diameter of 1.14 nm(diameter of supercage). Zeolite A has a void volume fraction of 0.47, with a Si/Al ratio of 1.0. The water molecules in the zeolite structure can be removed by dehydration and

their number is variable[45]. Actually, a typical feature of zeolites is that they can absorb and lose water without damage to their crystal structures.

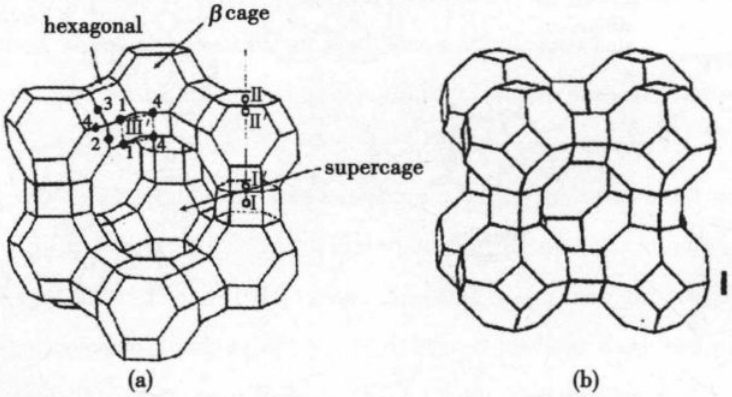

Figure 1.8 Structure of FAU type(a) and LTA type(b) zeolite[54]

1.1.2.3 Applications

Zeolites have uniform pore dimensions, high internal surface area, ion exchange ability, and high thermal stability. These properties make zeolites unique among other inorganic oxides. Zeolites have been accepted in a variety of applications, such as separation, catalysis and ion exchange[53-57]. The porous structure enables the zeolites to selectively admit some molecules while excluding those that are too large to fit into the pores. This leads to its molecular sieve properties. Zeolite as a molecular sieve was derived by McBain in 1932[55]. The dimensions of zeolites' channels and their ability to adsorb gases and water have made zeolite molecular sieves suitable for a number of applications such as in the areas of refinery fuel processing, production of chemicals and environmental pollution control[56-57].

Zeolites are also known as a shape selective catalyst. The possible shape selectivity of zeolites was illustrated in Figure 1.9. There are reactant selectivity, product selectivity and transition selectivity[53]. On the other hands, efficient optical properties of optically activated zeolites show various potential applications, such as fiber amplifiers, LEDs, biological probes, lighting, laser materials, and so on. In second part of this work, the photosensitization of RE ions by Ag clusters/ions in zeolites is studied, aiming for its potential application in white LEDs.

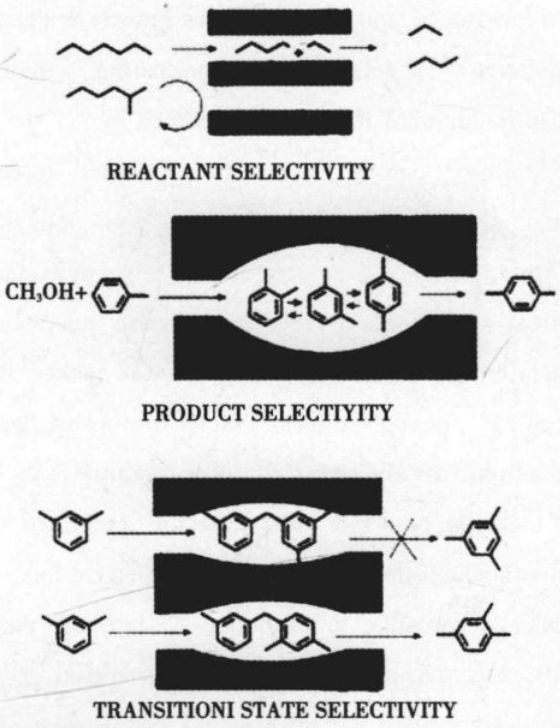

Figure 1.9 Schematic illustrations of shape selectivity exhibited by zeolites[53]

1.2 Luminescence centers in porous materials

1.2.1 Near infrared luminescence of Bi and rare earth ions in porous materials

1.2.1.1 NIR PL ofrare earth ions in porous silicon

One of the most considered host material is Si because of its relevance in the microelectronic and telecommunications industries. A promising alternative to the conventional Si doping procedures is to use porous Si layers as host. The large surface area allows the penetration of the luminescence centers into the matrix and the oxidation of the porous layers, which are necessary for the ion activation[58-61]. Porous Si is a very suitable host material for RE ions to utilize the sensitization effect of Si-ncs because it consists of many open pores. RE ions can be doped very easily

during the growth of porous Si and also after the growth. Several doping techniques such as ion implantation[58], spin-on[59], dip coating[60] and electrochemical[61] methods were used to incorporate RE ions into porous Si.

Recently, Er^{3+} doped porous Si has been studied intensively because the luminescence wavelength exactly coincides with the optical telecommunication wavelength[39-43]. Thus, Er^{3+} doped porous Si waveguide has been extensively investigated for optical amplifier applications. It shows many advanced properties, such as broad range of light transmission; porous Si makes Er^{3+} to be optically active; technology of Er^{3+} doped oxidized porous Si waveguides is compatible with standard Si microelectronic technology[39-43]. For example, V. P. Bondarenko[39] et al. investigated Er^{3+} doped oxidized porous Si for integrated optical waveguides, indicating that electrochemical deposition of Er in porous Si following the oxidation of the porous layer makes it possible to introduce Er into the core of the waveguide channel and preserve the waveguide properties of oxidized porous Si. It was also shown that Er^{3+} in the waveguide was in optically active state. PL at 1532 nm from Er^{3+} in optical waveguides can be observed by light pumping. Afterwards M. Balucani et al. reported Er-doped channel oxidized porous Si waveguides prepared from n-type Si by two-step anodization process[43]. It is found that the Er^{3+} doped oxidized porous Si waveguides can achieve the amplification effect by optimizing Er^{3+} concentration and refractive index of porous Si. These indicate that porous Si provides the possibility of fabricating a small size optical amplifier which can be integrated in thin film optical devices.

1.2.1.2 NIR PL of Bi inporous materials

The two useful wavelengths for optical communication in Si based material were shown in the Figure 1.10. One is minimum dispersion region of silica glass fiber at 1300 nm, the other is the maximum transparency wavelength of silica glass fiber at 1540 nm[62-63]. A method to solve the problem of lacking efficient silicon-based light source in optoelectronic integration on Si is luminescence centers doping. Considerable works have been contributed to develop optical fiber amplifiers to revolutionize the telecommunication systems, such as Erbium doped fiber amplifiers, Ytterbium doped fiber amplifiers, thulium doped fiber amplifiers, Praseodymium