Photoluminescence and Photoluminescent Excitation of Single Crystalline α-Si_3N_4 Nanobelts

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Abstract: single crystalline α-Si_3N_4 nanobelts synthesized via catalyst-assisted pyrolysis of polymeric precursor were investigated using absorption, photoluminescence (PL) and photoluminescent excitation (PLE). The optical absorption spectrum showed that the nanobelts exhibited indirect absorption behavior with optical band gap of ~5.0eV. Three broad peaks centered at 1.8eV, 2.3eV and 3.0eV were observed from PL spectrum of the nanobelts at room temperature. The PLE spectra suggest the existence of multi-fold energy levels within the gap.

Key words: single crystalline α-Si_3N_4; optical absorption; photoluminescence

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1 Introduction

Silicon nitride is a material widely used for microelectronic and optoelectronic application, such as charge storage layers[1,2] radiative elements in thin film light-emitting devices[3]. Similar to III-N semiconductors (e.g. GaN and AlN), crystalline silicon nitrides possess wide-band-gap semiconducting behavior and could be an excellent host material for its excellent thermo-mechanical properties, chemical inertness and high dopant concentration[4~6]. Recently, one-dimensional nanostucture of crystal silicon nitride such as nanobelt and wire developed quickly and opens potential applications of the materials in electronic/optic nanodevices[7~12]. Therefore, understanding of electronic/optic properties of silicon nitride is of a great interest. Previous studies on the optical properties of silicon nitride are primarily focused on its amorphous form[12~19]. While the optical properties of crystalline silicon nitrides were reported in a few previous studies[11,20], to the best of our knowledge, no detailed study on the subject has been reported, particularly on nanostructured silicon nitride.

In this paper, we report a detailed study on the optical properties of single crystal α-Si_3N_4 nanobelts.

2 Experimental

Crystalline α-Silicon nitride (α-Si_3N_4) nanobelts used in this study was synthesized by catalyst-assisted pyrolysis of a polysilazane polymeric precursor, as described previously[12]. The α-SiCN powders were reacted with catalyst ($FeCl_2$ in this study) to form Si-C-Fe liquid alloy droplets. The nanobelts were then precipitated and grew from the liquid droplets at 1250℃ under a flow of N_2.

Fig.1 is TEM images of the obtained nanobelts, which are 20nm~40nm in thickness, 400nm~1000nm in width. SEM shows it has a few hundreds of micrometers to several millimeters in length. X-ray diffraction and high-resolution electron transmission microscopy studies revealed that the nanobelts are single crystalline and α-Si_3N_4 phase[21]. optical properties of α-Si_3N_4 nanobelt are investigated by absorption spectra on UV-3100 double channel spectrometer, photoluminescence (PL) on UV-lamb micro-zone Raman spectrometer measured under the excitation of HeCd laser 325 nm line (E_{ex}=3.81eV), and photoluminescent excitation (PLE)

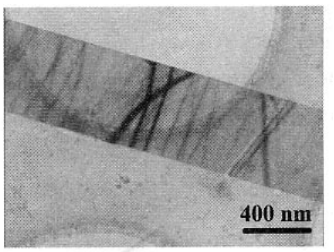

Fig.1 TEM images of the α-Si_3N_4 nanobelts

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3 Analysis and Discussion

To investigate nanobelts optical band, the optical absorption of the nanobelts was measured by mounting them on a quartz substrate. Fig.2a shows the relationship between absorbance α versus photon energy $\hbar\upsilon$. The spectrum shows that the nanobelts possess an absorption edge around 5.0eV, above which the absorption coefficient increases rapidly with photon energy. In addition, a weak absorption peak centered at 4.2eV can also be seen. Si_3N_4 is semiconductor with indirect band-gap, thus absorption coefficient is following[22]: $\alpha(\hbar\upsilon) = b_{abs}(\hbar\upsilon + E_{phonon} - E_{op-g})^2$.

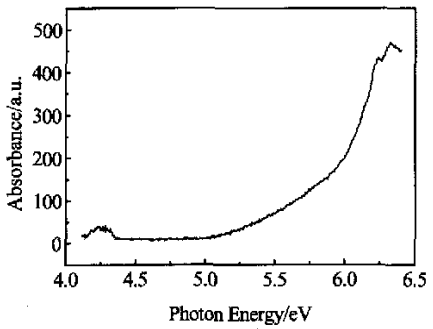

Fig.2 Transmission optical absorption spectra of the α-Si_3N_4 nanobelts

A linear relationship was observed between square root of absorbance and photon energy, and band gap is estimated to be 4.9eV by extrapolation. This value is closely consistent with theoretical result[23], where the extrapolated optical band gap of α-Si_3N_4 was calculated to be 5.0eV~5.2eV. Current result suggests that the nanobelts possibly contain lower amount of Si-Si defects in band gap, thus the intrinsic absorption can be revealed. The weak absorption peak at 4.2eV suggests the existence of such defects.

Intensive light-emission of the nanobelts was observed. Fig.3 is a typical PL spectrum of the nanobelts. The spectrum shows a broad emission band with the maximum at ~2.3eV. The broad band can be further split into three broad peaks by Gauss line-type peak fitting, centered at 1.8, 2.3 and 3.0eV, respectively. The similar PL behavior was observed for amorphous silicon nitride[13,14~16,23]. In these previous studies[14,16], the PL spectra of amorphous silicon nitride were explained by a model based on the Si-Si bonds separated by 4.6 eV. According to this model, the main broad PL peak at 2.3 eV~2.5eV was ascribed to the radiative recombination between electrons and holes in the Si-Si defect states and the metastable silicon-dangling bond (K^0 center). The transition at ~3.0eV occurs between electron/hole traps (with the trap depth between 1.3eV~1.5eV from the Si-Si defect states 4.6 eV for stoichiometry Si_3N_4, respectively[19]). The similarity between the PL spectra for the amorphous silicon nitride and the nanobelts suggests that it is likely that the same defects were involved in optical processes.

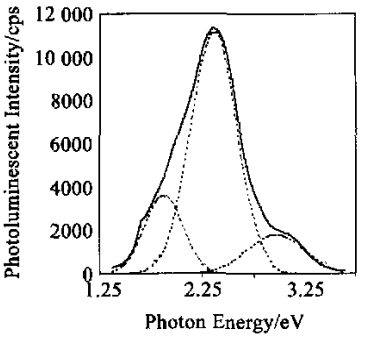

Fig.3 Photoluminescence of the Si_3N_4 nanobelts under excitation of 325nm at room temperature. Dots line shows the Gauss-fit peaks, centered at 1.8eV, 2.3eV and 3.0eV, respectively

In order to further understand the light emission processes, the luminescence of the nanobelts was measured as a function of excitation energy at selective detection energies. Fig. 4a and 4b show the PLE spectra with detection at 3.3 eV (e_1) and 1.8 eV (e_2), respectively. It can be seen that for both detections the maximum luminescence intensity occurs at the similar excitation energy; the onset energy is ~ 5.0 eV, which is consistent with the measured intrinsic optical gap (fig.2). This result suggests that the major contribution for the photoluminescence of the nanobelts is the transition between intrinsic band edges. Previous study[21] revealed that the photoluminescence of amorphous silicon nitride was dominated by the transition between Si-Si defect states. It is likely that the amount of Si-Si defects in the crystalline nanobelts is much less than that in amorphous Si_3N_4. Both PLE spectra appears to have a contribution from a peak at ~4.2eV, which is consistent with the weak peak observed in the absorption spectrum (fig.2). This result further suggests the existence of the transition at 4.2eV. The PLE spectrum for e_1 also contains a peak at ~4.6eV, which is not observed in the PLE spectrum for e_2. The 4.6eV transition could arise from Si-Si defect[14,16].

Robertson[24] has defined defects in silicon nitride to be of four types: Si—Si and N—N bonds, and Si and N dangling bonds. The Si—Si bond forms a bonding σ-orbital and antibonding σ^*-orbital that separated by 4.6eV for stoichiometry silicon nitride[14,16]. The silicon

dangling bond forms a defects state about the mid gap between σ-σ^*[24,25]. According to Robertson[24], besides the nitrogen dangling bond (N_2^0, N center), another type of nitrogen defect state can also give rise to levels within the Si-Si gap: namely N_4^+. The N_4^+ can be formed by reaction between positively charged silicon dangle bond and a bulk nitrogen ($Si_3^+ + N_3^0 = N_4^+ + Si_4^0$). Previous studies[16,26] suggested that the N_4^+ and N_2^0 defects form energy levels with the trap depth of 1.3eV~1.5eV from the Si-Si band edges, respectively.

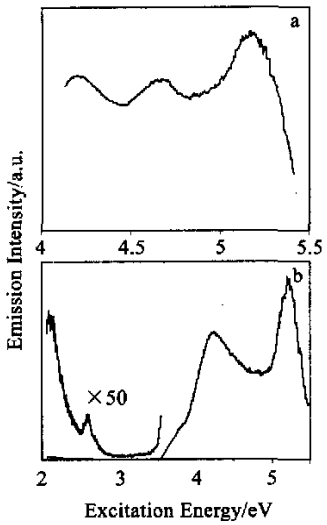

Fig.4　The photoluminescence excitation spectra of the α-Si_3N_4 nanobelts with detection at: (a) 3.3eV and (b) 1.8eV

Based on previous works, PL and PLE spectra can be rationalized that the PLE peak at 2.6eV for e_2 is possibly due to the double photons-absorption excitation from intrinsic valence edge to K^0 center and then to the intrinsic conduction edge. Since the probability for such double excitation is low, the contribution from 2.5eV peak is much lower than others.

In α-Si_3N_4 nanobelt with thickness of 20nm, the band-edge absorption spectra demonstrate optical absorption behavior of α-Si_3N_4 nanobelt follow the indirect gap absorption. The photoluminescence and photoluminescence excitation spectra illustrate that there are multifold kinds of impurities in α-Si_3N_4 nanobelt and their impurity energy level distribute in gap.

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α-Si_3N_4 单晶纳米带的光致发光及激发光谱研究

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摘　要：采用催化裂解有机前驱体方法制备出单晶α-Si_3N_4 纳米带，研究了纳米带的吸收光谱、光致发光（PL）及激发（PLE）光谱。吸收光谱表明约 5.0eV 禁带宽度的纳米带是间接带半导体吸收。室温下纳米带的 PL 光谱在 1.8eV, 2.3eV 和 3.0eV 处有 3 个宽峰。PLE 光谱显示在能隙中存在多个能级。

关键词：α-Si_3N_4；单晶；吸收；光致发光

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α-Si3N4单晶纳米带的光致发光及激发光谱研究

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