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Partial pressure-induced growth of silicon nitride belts with tunable width and photoluminescence property

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The α- and β-Si_3N_4 belts with tunable width were synthesized by regulating the partial pressure of NH_3/N_2 in the gaseous mixtures of Ar and NH_3/N_2 during the nitridation of silicon powders, which demonstrated a tunable photoluminescence property.

Introduction

The wide band-gap semiconductor materials with novel properties have exhibited promising applications in the fields of light emitting diode,[1, 2] laser[3, 4], field emission device,[5, 6] and so on. The performance of the functional devices strongly depends on the intrinsic properties and mircostructures of semiconductor materials.[7] Silicon nitride (Si_3N_4), as an important wide band gap (5.3 eV) semiconductor, has attracted extensive attention due to the unique physical and chemical properties including high mechanical strength, remarkable thermal and chemical stability, doping capability, tunable optoelectronic property.[8] Up to now, various morphologies of Si_3N_4, such as wire-like,[9, 10] belt-like[11-16], ring-like[17], have been prepared via nitridation of silicon powder[12], Fe-Si alloy,[13] silicon oxide[14], etc. But the controllable synthesis of Si_3N_4 structures with specific morphologies is still a challenge to meet the demand of functional devices. As known, the growth behaviors of materials strongly depend on the growth conditions, such as the growth temperature and the concentrations of reactants[18, 19]. For example, in anisotropic epitaxial growth model, these two factors can greatly influence the nucleation rate and the lateral growth rate of crystals.[20, 21] Recently, it is reported that the width of Si_3N_4 microribbons can be modulated in the range of 3 and 10 μm by controlling the nitridation temperatures of silicon monoxide (SiO) powders, leading to the tunable photoluminescence property in blue-light band.[22]

In this study, we obtain the Si_3N_4 belts with tunable width from nanoscale to microscale by regulating the partial pressure of NH_3/N_2 in the gaseous mixtures of Ar and NH_3/N_2, i.e. the concentrations of nitrogen-containing precursors, during the nitridation of silicon powders. When the partial pressure of NH_3/N_2 decreases from 100 to 2 %, the average width of Si_3N_4 belts can gradually increase from 183 to 2400 nm. The corresponding photoluminescence characterizations indicate the Si_3N_4 belts present tunable emission bands. Specifically, the Si_3N_4 belts with the width from 183 to 610 nm have strong cyan-red light emissions and show progressive blue shift, and the belts with 1675 and 2400 nm width have weak near ultraviolet-blue light emissions and very weak cyan-red light emissions.

Experimental

Si_3N_4 micro- and nano-belts were synthesized in a horizontal furnace by nitrifying silicon powders. In a typical run, the silicon powders, dispersed on an alumina wafer, were placed at the center of the furnace. The system was vacuumed by rotary pump to remove the O_2 and moisture. Subsequently, the system was elevated to 1400 °C in 50 sccm (standard cubic centimeter per minute) gas mixtures of NH_3/N_2 (4 vol.% NH_3) and Ar at the rate of 10 K min^{-1}, and then kept for 14 h. The volume ratios of NH_3/N_2 and Ar are specified as 100:0, 50:50, 40:60, 10:90, 2:98, 0:100. Finally, the system was cooled down to ambient temperature. The structures and morphologies of the products were characterized by X-ray diffraction (XRD, D8 Advance A25, Co target, $\lambda_{K\alpha I}$=1.78897 Å), scanning electron microscopy (SEM, Hitachi S-4800) attached with an energy-dispersive X-ray spectroscopy (EDS, Ametek, EDAX-Genesis-XM2-Imaging-60SEM), and high resolution transmission electron microscope (HRTEM, JEOL, JEM-2100, operating at 200 kV). The photoluminescence properties were investigated by FLS 920 with a He-Cd laser of 325 nm at room temperature.

Results and Discussion

Fig. 1 presents the XRD patterns of the nitridation products under different ratios of $P(NH_3/N_2)$ and P(Ar). As shown in Fig.1, all five samples include the hexagonal Si_3N_4, indexed to α and β phases. The ratios of β and α are near 1.2 (Fig. S1, ESI† SI-1), which is basically independent of the partial pressure of NH_3/N_2 in the gaseous mixtures of Ar and NH_3/N_2. For the samples nitrified at $P(NH_3/N_2)$:P(Ar)=100:0 and 50:50, all diffraction peaks are assigned to Si_3N_4 without Si signals while there are the additional diffraction peaks of Si in the samples nitrified at $P(NH_3/N_2)$:P(Ar)=40:60, 10:90, and 2:98. The Si signals come from incomplete nitridation of Si powders.

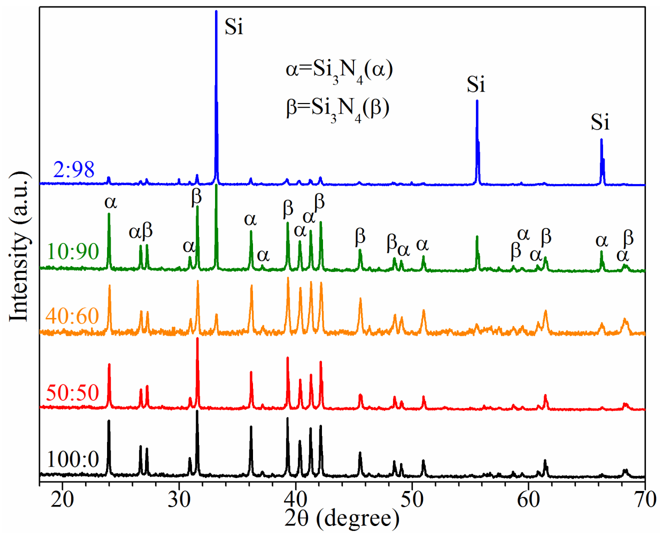

Fig. 1 XRD patterns of the nitridation products at $P(NH_3/N_2):P(Ar)$=100:0, 50:50, 40:60, 10:90, 2:98. Co target, $\lambda_{K\alpha 1}$=1.78897 Å

The typical morphologies of the products nitrified at different ratios of $P(NH_3/N_2)$ and P(Ar) are shown in Fig. 2 and Fig. S2 (ESI† SI-2). It can be clearly seen that all five products show the belt-like morphology, whose statistic width are centered at 183, 345, 610, 1675, and 2400 nm with the full width at half maximum (FWHM) of 102, 117, 279, 500, and 894 nm corresponding to the ratios of $P(NH_3/N_2)$ and P(Ar) at 100:0, 50:50, 40:60, 10:90, 2:98 (Fig. 3c, f, i, l, o). Namely, with decreasing

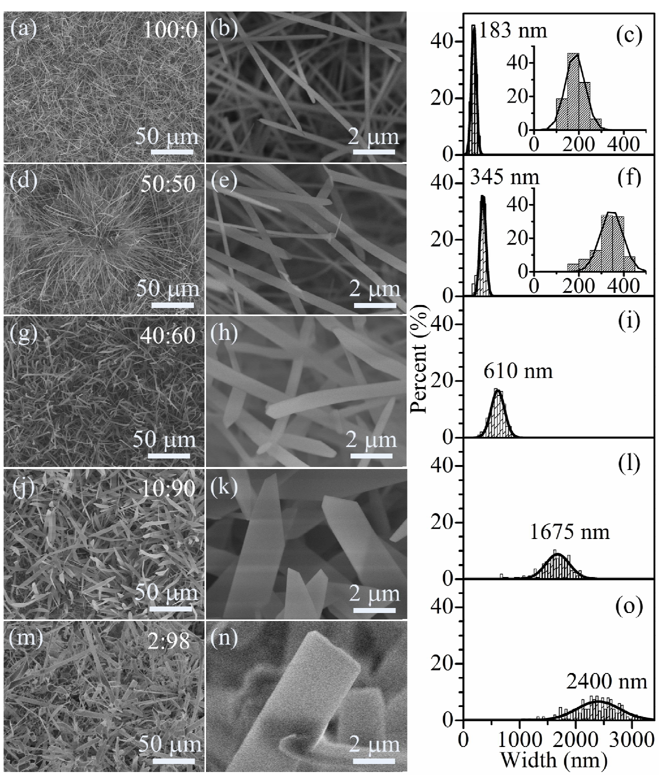

Fig. 2 Typical SEM images and width distribution of the products obtained in different ratios of $P(NH_3/N_2)$ and P(Ar), i.e., 100:0, 50:50, 40:60, 10:90, 2:98. Histograms in (c, f, i, l, o) are fit with Gaussians and the peak centers are labeled.

the ratio of $P(NH_3/N_2)$ and P(Ar), the width of the belts increases from several hundred nanometers to several microns and the width distribution becomes wider and wider. When the silicon powders were treated in pure Ar flow ($P(NH_3/N_2)$:P(Ar)=0:100), no wire-like or belt-like morphologies can be observed (Fig. S2f, ESI† SI-2). Further EDS and element mapping evidences from a single micro-belt demonstrate the belt is consisted of Si and N elements (Fig. S3, ESI† SI-3). In addition, the influences of the nitridation temperature are investigated. At the designated $P(NH_3/N_2)$:P(Ar)=50:50, with elevating the nitridation temperatures from 1300 to 1400 ^oC, the average width of the belts increases slightly from 270 to 345 nm (Fig. S4, ESI† SI-4). Thus, following Fig. 2 and Fig. S4, modulating the partial pressure is an effective way to control the width of belts during the nitridation of silicon powders.

To investigate the microstructure of the nitridation products, (HR)TEM observations were carried out. The typical TEM image of the nitridation product at $P(NH_3/N_2)$:P(Ar)=50:50 indicates that the belts are ca. 200-300 nm in width (Fig. 3a). The corresponding HRTEM image in Fig. 3b shows the interplanar spacings of 4.4 and 2.9 Å with the angle of ca. 83^o, corresponding to the d_{0-11} and d_{201} of hexagonal α–Si_3N_4 with the dihedral angle of 83^o. Besides, there exist some defects on the surface of belt. In combination with XRD analyses, SEM and (HR)TEM observations, EDS and element mapping results, the belts can be assigned to Si_3N_4.

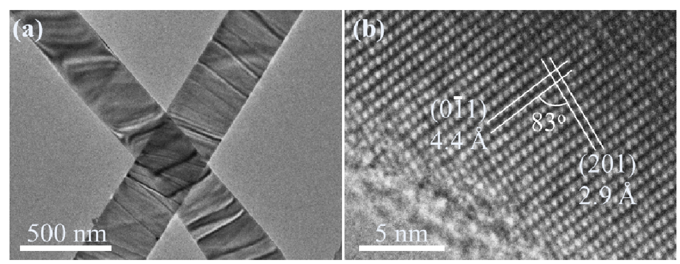

Fig. 3 TEM (a) and HRTEM (b) images of the products obtained at $P(NH_3/N_2)$:P(Ar)=50:50.

As demonstrated in Fig. 2, the width of Si_3N_4 belts strongly depends on the partial pressure of NH_3/N_2 in the gaseous mixtures of Ar and NH_3/N_2. To understand the relationship between the width of Si_3N_4 belts and the partial pressure of NH_3/N_2 in the gaseous mixtures of Ar and NH_3/N_2 at the designated nitridation temperature (e.g. 1400 ^oC), the formation schematic diagram of Si_3N_4 belts is proposed (Fig. 4). Generally, for anisotropic epitaxial growth of compound materials, e.g. Si_3N_4, they are firstly nucleated on the substrate and then epitaxially grown into a variety of morphologies due to the difference of axial and lateral growth rate[23, 24]. In our case of partial pressure-induced growth of Si_3N_4, with increasing the partial pressure of NH_3/N_2, the nucleation density of Si_3N_4 increases and the axial growth rate increases faster than the lateral one. Hence, the higher ratio of $P(NH_3/N_2)$ and P(Ar) is, the thinner Si_3N_4 belts are formed. In other words, the size and density of Si_3N_4 belts can be regulated by a facile method of controlling the partial pressure of NH_3/N_2 in the gaseous mixtures of Ar and NH_3/N_2. In addition, with elevating the nitridation temperatures from 1300 to 1400 ^oC, the lateral growth rate increases slightly, which leads to the slight increase of the Si_3N_4 belts.

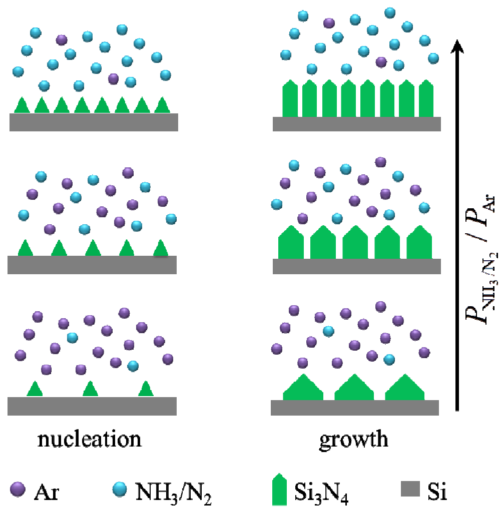

Fig. 4 The formation schematic diagram of Si_3N_4 belts with adjustable width. With increasing the partial pressure of NH_3/N_2 in in the gaseous mixtures of Ar and NH_3/N_2, the width of Si_3N_4 belts decreases.

The photoluminescence properties of the five Si_3N_4 samples are investigated by PL technique at room temperature under excitation of 325 nm. As shown in Fig.5 and Fig. S5 (ESI† SI-5), all five Si_3N_4 samples exhibit the broad emission bands in near ultraviolet (UV)-visible light region (350-680 nm). Specifically, for the three samples of Si_3N_4 belts with the average width of 183, 345, and 610 nm, there exist the intensive cyan-red emission bands with progressive blue shift and the weak near UV-blue emission bands. For other two samples of Si_3N_4 belts with the average width of 1675 and 2400 nm, the emission bands mainly locate at near UV-blue light region while the cyan-red emission bands are very weak. The emissions can be attributed to the defect energy levels in the Si_3N_4 belts, including Si-Si, N-N, ≡Si and =N.[25-28] However, the mechanism of the variable emission bands related with the width of Si_3N_4 belts is still unclear and the further investigation is underway.

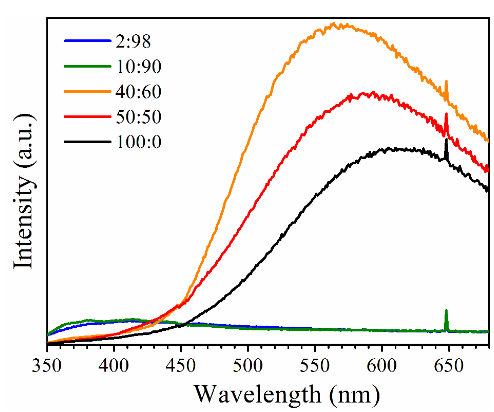

Fig. 5 PL spectra of the Si_3N_4 products. The sharp peaks near 650 nm come from the multiplication frequency of 325 nm excitation.

Conclusions

In summary, the width of α- and β-Si_3N_4 belts with good crystallinity can be effectively tuned by regulating the partial pressure of NH_3/N_2 in Ar-NH_3/N_2 flow during nitridation of silicon powders. With increasing the partial pressure of NH_3/N_2 in the gaseous mixture of Ar and NH_3/N_2, the average width of Si_3N_4 belts decreases from several microns to several hundred nanometers and the width distribution becomes narrower and narrower. The Si_3N_4 belts exhibit the broad emission bands in near UV-visible light region (350-680 nm), attributed to the defect energy levels such as Si-Si, N-N, ≡Si and =N. Specifically, the Si_3N_4 belts with the average width lower than 610 nm have the intensive cyan-red emission bands while, for the belts with average width in micron scale, the cyan-red emission bands are very weak. This provides a facile method to synthesize compound semiconductor materials with tunable morphology and optic property.

Acknowledgements

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Notes and references

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Graphic Abstract

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