ESR PROPERTIES OF SILICON NITRIDE NANORODS

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We prepared Solid silicon nitride nanowires using carbon nanotubes as precursors., Si and SiO_2 were used as raw materials, the reaction was carried out in ammonia atmosphere The structure, phase composition, ESR properties and oxidation resistance of the sample were investigated. The results showed that the sizes of the nanorods are 60–80 nm in diameter and up to several microns in length. In the products α-Si_3N_4 is the main component; the FTIR spectra of the silicon nitride nanowires have blue shift phenomena;The ESR properties show that the as made materials contains a large number of unpaired electrons

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1. Introduction

Silicon nitride and its derivative sialon ceramics continue to be subjected to the sustained attention of ceramics research groups worldwide[1]. Although earlier hopes of utilizing the excellent thermomechanical properties of these materials in such demanding applications as gas turbines were not realized[2,3], the advancements of the last decade have led to implementation of silicon nitride materials in cutting tools[4], bearings[5], turbochargers[6], engine valves[7] and other wear-resistant components[8].

Compared with nanopowders(0 dimensional nanomaterials), the synthesis of one dimensional structure nanomaterials still remain a challenge. Since the discovery of carbon nanotube[,9], efforts have been made on synthesis of one dimensional nanoscale materials by using carbon nanotubes as the precursors. L.T. Sun [10] who prepared the diamond nanowires use CNTs-templated method and proposed a model for growth mechanism of nanorods. Han[11] reported that they synthesized SiC nanorods in a two-step process involving the generation of SiO followed by reacting with carbon nanotubes under N_2 atmosphere. In this paper, we developed a method fabricate Si_3N_4 nanowires using carbon nanotubes as the precursor and ammonia as a reaction gas. This method can prepare Si_3N_4 nanowires at low temperature, which make the production low cost.

2. Experimental

2.1. Synthesis of silicon nitride nanowires

In the first step, the MWCNTs were purified by concentrated sulfuric acid, the CNTs (1.5 g) were boiled for 24 h in 100 ml 95 wt% H_2SO_4 under fluxing; Then they were washed with water

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and dried at 80 ^{o}C for 24 h. The mixture of silicon and silicon dioxide powder were spread on the Al_2O_3 boat, and covered with as treaded carbon nanotubes to react. The reaction was carried out at 1500 K for 1 h, at the same time ammonia gas was fed into the tube at a flow rate of 50 sccm to maintain the reactant pressure. After reaction for several hours, the specimens were cooled down in nitrogen. Finally a white woollike material formed at the original nanotube bed.

2.2. Characterization

A X-Ray Diffraction(XRD) with Cu Kα radiation was used at room temperature to identify the phase and the crystal structure. The micro-structure of carbon coated iron nanoparticles was observed by using transmission electron microscope (TEM)(JEM-2010 HR) operating at 200Kv. Q600 DSC / TGA simultaneous, TA companies in the United States was employed to test DSC / TGA .Test conduction: weight between 1.5-2.0 mg, carrier gas is air, heating rate 20 ^{o}C / min, from room temperature to 800 ^{o}C. A Fourier transform infrared spectroscope was used to examine the surface bond of the nanowires. The dielectric constant of the products was measured using multi-frequency meter (HP-4294A).

3. Results and discussion

3.1. Phase analysis

Fig. 1 is an XRD pattern of the products, we can see that only α-Si_3N_4 phase and β-Si_3N_4 phase are detected by X-ray. As can be seen from Fig. 1, the peaks assigned to α-Si_3N_4 (20.5° , 26.6°and 30.9°)are stronger than that of β-Si_3N_4, which indicate the products are mainly α-Si_3N_4. At the same time we can see that there is no peak associated with silicon carbide, graphite, or other crystalline in the XRD pattern.

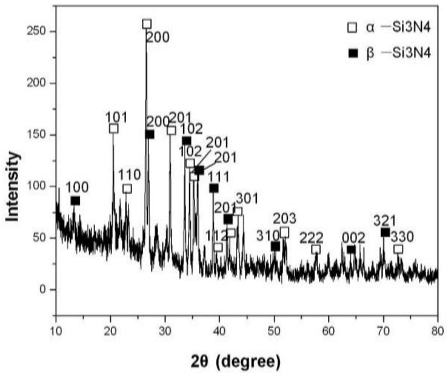

Fig. 1. X-ray diffraction spectrum of silicon nitride nanorods

3.2. Structural and morphology of silicon nitride nanowires

Fig.2(a,) are the TEM micrographs of the products-silicon nitride nanowires. They are solid other than the hollow core structure of nanotubes. The diameters of the produced nitride nanowires(about 60-80nm) are significantly larger than the carbon precursors. Fig. 2(b) shows the growth of nitride nanowires in the carbon nanotube(40-60nm), it can be seen that nitride start grow at the outlet of the carbon nanotubes. This phenomenon can be expressed simply as follows:

3.3 FTIR spectra of silicon nitride nanowires

a) b)

Fig. 2. TEM micrographs of silicon nitride nanowires(a, silicon nitride nanowires; b, growth of silicon nitride nanowire)

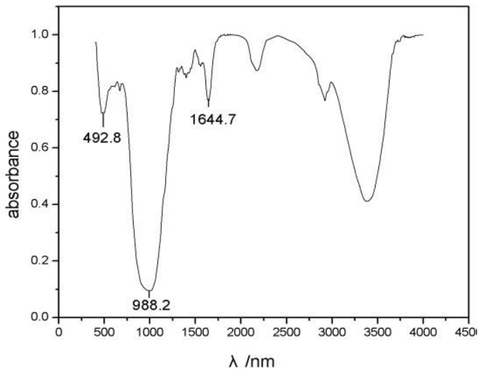

Fig.3. FTIR spectra of the silicon nitride nanowires

The FTIR spectra of the silicon nitride nanowires are shown in Fig. 3, the sample have three main peaks., the peak at 492.8cm-1 is stretching motion of N-Si bonds, the peak at 1644.7cm-1 is flexural vibration of the N-Si bonds, the Si=O stretching bond is observed near 998cm-1. Comparison with block nitride peaks at 481.3 cm-1，989cm-1 and 1599 cm-1 [16]. The infrared spectrum of nano-structure materials has a blue shift phenomena. The reason is that the nano-material's quantum size effects lead to blue shift. Nano-materials have great surface area, surface atoms will have defects and lattice distortion, the bond length of surface atoms different to the body atoms, which makes the nanowire's blue shift of infrared absorption spectrum.

3.3. ESR propriety of silicon nitride nanowires

Fif.4 is the ESR curves of silicon nitride nanowires from 100K-280K, as we can see that at all the temperature range , the ESR spectrum showed obvious symmetrical shape, and the at low temperature(100K) the ESR curves show Higher spectral intensity, this means that at low temperatures, silicon nitride nanowires contains more unpaired electrons.

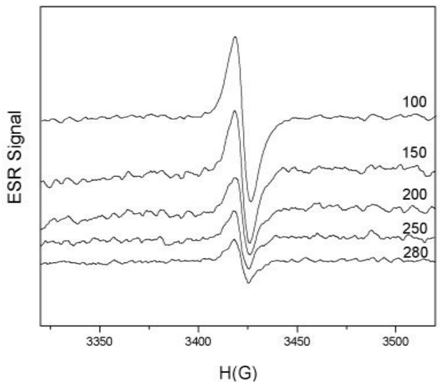

Fig.4 ESR curves of silicon nitride nanowires at different temperature

4. Conclusions

Silicon nitride nanowires are fabricated using carbon nanotubes as precursors, and the samples mainly are α-Si_3N_4 and β-Si_3N_4. α-Si_3N_4 ; different from the nanotubes, the silicon nitride nanowires are solid materials, at the same time the diameter of nitride is larger than the nanotubes; the sample shows good oxidation resistance, only a little of the nitride can be oxidized in high temperature; The ESR proprieties low temperatures, silicon nitride nanowires contains more unpaired electrons than that of high temperature.

Acknowledgments

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