Low-Temperature Solid State Synthesis and Characterization of Superconducting Vanadium Nitride *

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(Received 12 November 2016)

Superconducting vanadium nitride (VN) is successfully synthesized by a solid-state reaction of vanadium pentoxide, sodium amide and sulfur in an autoclave at a relatively low temperature (240–400°C). The obtained samples are characterized by x-ray diffraction, x-ray photoelectron spectroscopy and transmission electron microscopy. The result of the magnetization of the obtained VN product as a function of temperature indicates that the onset superconducting transition temperature is about 8.4 K. Furthermore, the possible reaction mechanism is also discussed.

PACS: 81.16.Be, 77.84.Bw, 87.64.Bx DOI: 10.1088/0256-307X/34/2/028101

Over half the past century, metal nitrides, especially those of transition metals, have attracted considerable attention for their attractive chemical and physical properties, such as high melting point, extreme hardness, high chemical stability, excellent oxidation stability and high thermal conductivity.[1–3] Thus transition metal nitrides have been applied in many fields. Among transition metal nitrides, vanadium nitride (VN) materials have received increasing attention owing to their unique properties. VN can be utilized as abrasive materials and cutting tools for its high hardness.[4] VN could also be used as a practical catalyst because of the high catalytic activity and selectivity similar to those of noble metals.[5] In recent years, VN films have delivered excellent electrochemical property as an anode for rechargeable lithium ion batteries.[6] Moreover, VN is a superconductor with a transition temperature of 6–9 K.[7,8]

Up to now, different methods have been reported to prepare VN materials. For example, VN can be produced by carbothermal reduction of vanadium pentoxide in N_2 at about 1500°C.[9] VN can also be prepared by heating metal powder in N_2 flow at about 1350°C.[10] Chu *et al.* have reported the preparation of VN by reactive magnetron sputter deposition.[6,11] VN materials have been synthesized by ammonolysis of metal chlorides, oxides, or sulfides at 800–1400°C.[12–14] Dai *et al.* reported the preparation of VN thin film by pulsed laser deposition (PLD).[15] Solid state metathesis (SSM) and self-propagating high temperature synthesis (SHS) can also be used to synthesize VN materials.[16,17] Qian *et al.* have synthesized VN materials by a chemical reaction of vanadium chloride and sodium azide at 600°C in an autoclave.[18,19] VN materials have been prepared by mechanochemical synthesis, the microwave-assisted combustion method and other methods.[20–25] Recently, transition metal nitride films have been prepared by using the plasma focus device.[26,27]

In this Letter, a sulfur-assisted solid state approach is developed for the preparation of VN. The preparation of VN is carried out in an autoclave at 240–400°C by solid state metathesis of vanadium pentoxide, sulfur and sodium amide. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HR-TEM) are used to investigate the crystal structures and morphologies of the obtained products. In addition, the magnetization of the obtained VN sample is characterized by a superconducting quantum interference device (SQUID).

All manipulations are carried out in a glove box purged with nitrogen gas to prevent oxygen contamination. In a typical procedure, V_2O_5 (0.45 g), S (0.32 g) and excess $NaNH_2$ (3.20 g) are put into a stainless-steel autoclave of 20 mL capacity. Then the autoclave is sealed and heated from room temperature to the target temperature (240°C, 300°C and 400°C) at a rate of 10°C/min in an electric stove and kept for 20 h. After it has naturally cooled to room temperature, the raw product is washed with ethanol, distilled water and hydrochloric acid (1 mol/L), finally it is dried in a vacuum oven at 50°C for 8 h. The obtained samples at 240°C, 300°C and 400°C are labeled as

*Supported by the Natural Science Foundation of Jiangsu Province under Grant No BK20160292, the Natural Science Foundation of the Higher Educations Institutions of Jiangsu Province under Grant No 16KJB150013, the National Natural Science Foundation of China under Grant No U1404505, and the Program for Innovative Talent in University of Henan Province under Grant No 16HASTIT010.

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samples 1, 2 and 3, respectively.

X-ray diffraction (XRD) measurement is carried out with a Philips X'pert x-ray diffractometer (Cu $K\alpha$ $\lambda = 1.54178$ Å). The scanning electron microscopy (SEM) images are taken by using a field-emission scanning electron microscope (FE-SEM, JEOL-JSM-6700 F). The transmission electron microscopy (TEM) image and high-resolution transmission electron microscopy (HRTEM) image are taken on a JEOL-2010 transmission electron microscope with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) is performed on an ESCA-Lab MKII x-ray photoelectron spectrometer, using Mg $K\alpha$ x-ray as the excitation source. The zero field-cooled magnetization is collected from a SQUID magnetometer (MPMS, Quantum Design) from 2 to 30 K with an applied field of $H = 10$ Oe.

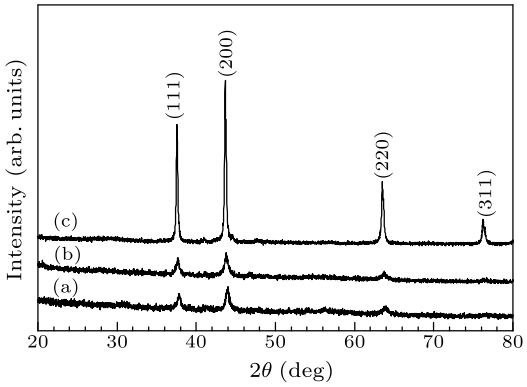

Fig. 1. Typical XRD patterns of the VN samples: (a) sample 1 (obtained at 240℃), (b) sample 2 (obtained at 300℃), and (c) sample 3 (obtained at 400℃).

The phase identification of the obtained samples is carried out using the XRD pattern. The XRD patterns of the obtained samples are shown in Fig. 1. The XRD patterns of samples 1 and 2 (shown in Figs. 1(a) and 1(b)) both have three diffraction peaks, which can be indexed as (111), (200) and (220) diffraction planes of cubic vanadium nitride (JCPDS Card Files, No. 78-1315). Figure 1(c) shows the XRD pattern of sample 3. Four peaks located at 37.56°, 43.67°, 63.49° and 76.22° can be found in Fig. 1(c), which can also be indexed as (111), (200), (220) and (311) diffraction surfaces of cubic vanadium nitride. The refinement gives the cell constant, $a = 4.144$ Å, which is in good agreement with the reported value for cubic VN ($a = 4.137$ Å, JCPDS Card No. 78-1315). No obvious evidences of impurities such as metal vanadium and vanadium oxide can be found in the XRD patterns, which indicate that the obtained samples are cubic VN with high purity. The diffraction peaks in the XRD pattern of the sample obtained at 400℃ become narrower, which indicate that the grain size of the sample obtained at 400℃ is larger than that of the samples obtained at 240℃ and 300℃.

The morphologies of the obtained samples at different temperatures are investigated by FE-SEM and TEM. Figures 2(a) and 2(b) show the FE-SEM images of samples 1 and 2, respectively. It can be seen that the VN samples obtained at 240℃ and 300℃ are composed of particles with average sizes of about 30 nm and 50 nm, respectively. The FE-SEM and TEM images of sample 3 are shown in Figs. 3(c) and 3(d), respectively. From Figs. 3(c) and 3(d), VN octahedral particles with a diameter of about 150 nm are observed in sample 3. The HRTEM image of sample 3 (shown in the inset of Fig. 3(d)) shows that the measured lattice spacing of 0.24 nm matches well with the (111) plane of VN, which indicates that the VN samples obtained at 400℃ are well crystallized.

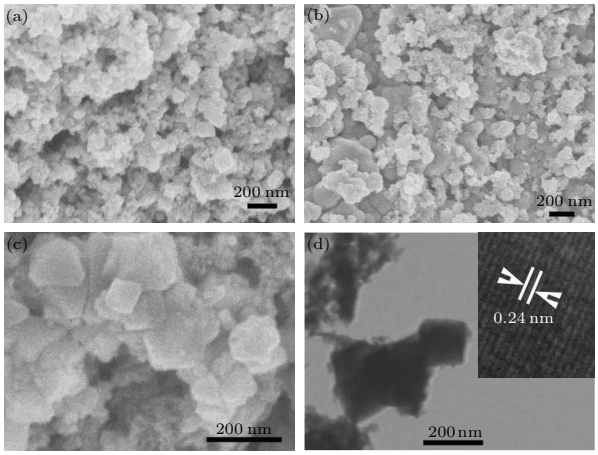

Fig. 2. FE-SEM images of (a) sample 1, (b) sample 2 and (c) sample 3. (d) The TEM image of sample 3, with the inset being the HRTEM image.

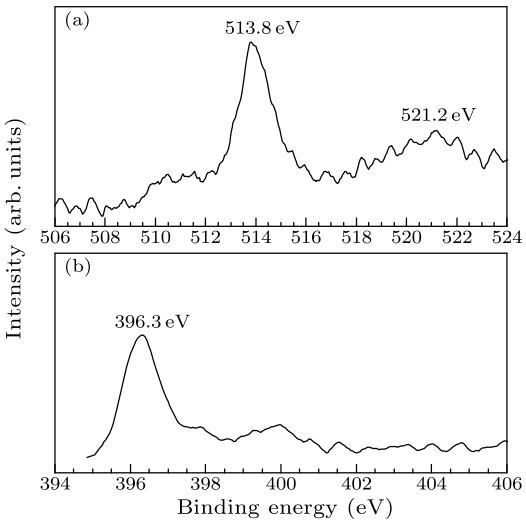

Fig. 3. XPS spectra of sample 3: (a) V $2p$ spectrum and (b) N $1s$ spectrum.

XPS can also be used to investigate the surface composition of the obtained VN sample. Figure 3 shows the XPS spectra of the VN sample obtained at 400℃. The V $2p$ and N $1s$ core-level regions are ex-

amined. The peaks at 513.8 eV and 521.2 eV (shown in Fig. 3(a)) correspond to V $2p3/2$ and V $2p1/2$ binding energy of VN, respectively. The peak at 396.3 eV (shown in Fig. 3(b)) corresponds to N $1s$ binding energy of VN in the literature. These results are close to the reported values for bulk vanadium nitride.[28]

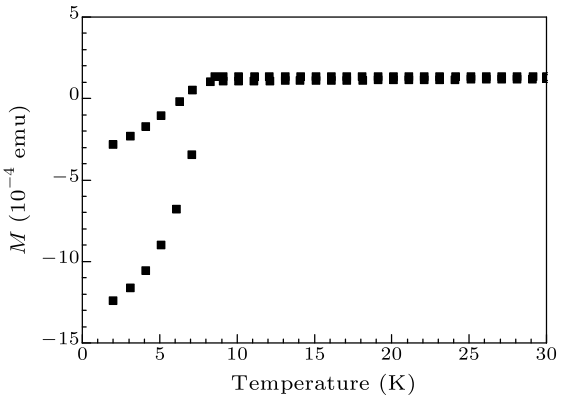

Fig. 4. Temperature dependence of magnetization for sample 3.

The magnetic measurements of the obtained VN sample are carried out at 2–30 K and $H = 10$ Oe using a SQUID magnetometer (MPMS, Quantum Design). The magnetization of sample 3 as a function of temperature is plotted in Fig. 4, under conditions of zero field cooling (ZFC) and field cooling (FC) at 10 Oe. The clear onset of a strong Meissner effect can be observed, which confirms the existence of superconductivity in the obtained VN materials and indicates that the superconducting transition temperature T_c for the VN sample is 8.4 K. It is also found that the diamagnetism observed in the ZFC is obviously larger than that under FC conditions. This may result from the existence of flux trapping in the superconductor under FC, which causes the irreversibility of the magnetization curve.

The solid state route to prepare cubic VN is essentially based on a chemical reaction of sodium amide, vanadium pentoxide and sulfur. Sodium amide as a nitrogen source with high reactivity has been widely used in the preparation of metal nitride. However, without the assistance of elemental sulfur, vanadium nitride cannot be obtained by the reaction of sodium amide and vanadium pentoxide at 240℃ in an autoclave, the chemical reaction between sodium amide and vanadium pentoxide is initiated at a high temperature of 600℃. Thus elemental sulfur has participated in the formation of the cubic phase VN nanocrystalline. With the assistance of sulfur, cubic phase VN can be obtained at 240℃, in which the exothermic reaction between sulfur and sodium amide led to produce cubic phase VN at a relatively low temperature (Eq. (1)). It is generally known that sodium amide transforms to Na_3N by loss of ammonia under heating conditions (Eq. (2)).[29] Then, the renascent Na_3N react with V_2O_5 to produce cubic phase VN (Eq. (3)). Furthermore, the reaction temperatures play another key role in the preparation of cubic phase VN. When the reaction temperature is below 230℃, no cubic phase VN can be obtained under the present experimental conditions. It is shown that with the increase of the reaction temperature in the process, the sizes of the obtained samples grow larger with high crystallinity. The mole ratio of the raw materials used in this process is V_2O_5:S:$NaNH_2$=2:5:40. Proper excess of $NaNH_2$ used in the process is necessary to guarantee the conversion of V_2O_5 to cubic phase VN completely at the reaction temperature. Based on the above-mentioned experimental results, the overall chemical reaction formulas are expressed as follows:

$$6NaNH_2 + 3S = 3Na_2S + 4NH_3 + N_2, \quad (1)$$

$$3NaNH_2 = Na_3N + 2NH_3, \quad (2)$$

$$10Na_3N + 3V_2O_5 = 15Na_2O + 6VN + 2N_2, \quad (3)$$

$$30NaNH_2 + 2V_2O_5 + 5S = 10Na_2O + 4VN + 3N_2 + 5Na_2S + 20NH_3. \quad (4)$$

In conclusion, a simple solid-state approach has been developed for the preparation of nanocrystalline VN at 240–400℃ in an autoclave. The sizes of the VN samples obtained at different temperatures are investigated by XRD and SEM. The onset superconducting temperature for the VN sample obtained at 400℃ is observed at 8.4 K. This synthetic route can be extended to prepare other transition-metal nitrides at relatively low temperature.

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