Uranium Nitride U_2N_3 as a novel thermoelectric material

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Abstract

Uranium compounds are potential candidate materials for thermoelectric power generation and applications in environmentally-friendly cooling. In the present study, single phase U_2N_3 compound synthesized by glow plasma nitriding is reported as a thermoelectric material for the first time. The electrical conductivity is 302 S/cm at 243 K which decreases to 202 S/cm with increasing temperature, indicating the semimetallic behavior. The Seebeck coefficient of U_2N_3 suggests *n*-type conduction with the absolute value of 87 μ V/K at 243 K and 133 μ V/K at 383 K. The strong scattering of conductive electrons by the 5f electrons of uranium near the Fermi level vicinity is considered to attribute to the large Seebeck coefficient. The maximum Power factor is 3.58 μ Wcm⁻¹K⁻² obtained at 383 K, one order of magnitude larger than that of uranium borides.

Key words: U_2N_3 , Microstructure, Electrical properties

1. Introduction

Thermoelectric materials have received renewed attentions for their potential applications in environmentally-friendly cooling and power generation based on the direct energy conversion between

heat and electricity [1, 2]. Theoretically, an efficient TE materials must exhibit a high thermoelectric dimensionless Figure of Merit, $ZT = \alpha^2 \sigma T / \kappa$, where α indicates the Seebeck coefficient, σ indicates the electrical conductivity, T indicates the absolute temperature, and κ is the thermal conductivity consisting of carrier (κ_e) and phonon (or lattice κ_L) components.

After simplification, ZT is in proportion to $m^{2/3}(\mu_c / \kappa_L)$ [3], where m is the charge carrier effective mass and μ_c is the mobility of charge carrier. Generally, materials with large atomic number lead to higher $m^{2/3}(\mu_c / \kappa_L)$, and the f-electrons tend to result in large charge carrier mass [4]. Since the high atomic number (92) and 5f-electrons of uranium element, during the last few years, there have been considerable interests in the research of uranium compounds. Bando [5] found that the Seebeck coefficient of UNi_4B , UPt_2In and $UCu_{3+x}Ga_{2-x}$ ranged from 16~70 $\mu V/K$ at room temperature. They proposed that the rather large α was mainly ascribed to the strong scattering of conductive electrons by the 5f electrons near the Fermi level vicinity. Djerassi [6] and Ruello [7] investigated the electrical transport properties of two types of uranium oxide, UO_2 and U_3O_8 . The Seebeck coefficient of uranium oxides both presented a p to n transition at high temperature due to the extrinsic to intrinsic transition, which was unfavorable to obtain the high absolute value of α . As for uranium borides, Yamamoto [8], Nishi [4], and Troć [9] were focused on the good-performing thermoelectric properties of the UB_2 , UB_4 and UB_{12} , respectively. With respect to the uranium nitrides, there are three kinds of stable phases along with the increase of the N/U atomic ratio, which are UN , U_2N_3 and UN_2 . The thermoelectric properties of UN have already been preliminarily studied by Samsel-Czekala et al [10]. However, U_2N_3 and UN_2 with higher nitrogen content have not yet been concerned as thermoelectric materials so far as we know.

Thus, the purpose of the present work is focused on the U_2N_3 phase on both microstructure and

thermoelectric properties. The electrical conductivity and Seebeck coefficient are measured from 243 to 383 K temperature range.

2. Experimental procedures

The fabrication of U_2N_3 was carried out in a self-designed nitriding furnace that was described elsewhere [11]. High purity uranium metal flakes were used as starting materials. In order to remove the oxide layer, the sample surface was mechanically ground and polished before it was transferred into the vacuum chamber (10^{-4} Pa). Then 50 Pa nitrogen (99.99% purity) was fed into the vacuum chamber. The pulse bias between the uranium flake and chamber wall was -900 V with 40 kHz frequency and 20% duty cycles to forming the glow discharge. Meanwhile, the sample was heated at 350 °C for 90 min to accelerate the diffusion of N. After nitriding, the uranium nitride film samples were deposited on Al_2O_3 ceramic substrates by hollow cathode sputtering. The purpose we deposit uranium nitride film to the alumina substrate is to avoid the metal uranium effects on the electrical properties. After nitriding, the thickness of uranium nitride layer is about several microns forming on the surface of metal uranium. Therefore, we need to deposit single phase uranium nitride on an insulating alumina substrate with little impact on the electrical properties.

The phase composition of the samples was identified by X-ray diffraction (XRD) on X'Pert Pro system with Cu-K_α radiation. The elemental composition was detected via Phi650-SAM system by Auger electron spectroscopy (AES) depth profiles analysis. Scanning electron microscopy (SEM, FEI Sirion200) was used to observe the morphologies. Before the XRD, SEM as well as AES characterization, the specimens were carefully cleaned with ethanol, acetone and deionized water, then dried with compressed air. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy

(HRTEM) was performed on a FEI Titan with an accelerating voltage of 200 kV. For the TEM characterization, the two specimens were pasted by Gatan G1 epoxy resin adhesive with the films face to face. Cross-section samples with 500 μm in thickness were cut, mounted and mechanically polished to 20-30 μm in thickness. After about 10 h ion beam milling, the TEM sample with enough electron transparent area is obtained. Electrical conductivity and Seebeck coefficient were measured in the temperature range of 243 K to 383 K via Quantum Design physical property measurement system (PPMS). Four Cu straps probes were electrically attached to the specimens via silver conductive adhesive paste to test the electrical conductivity. Seebeck coefficient was measured by the middle two probes which were used to explore potential difference.

3. Results and discussion

3.1 Microstructure and composition

The XRD patterns of nitriding samples are shown in Fig.1. All the peaks can be indexed by α - U_2N_3 phase with bcc Mn_2O_3 -type structure (JCPDS 15-426, as shown in Fig.1 (a)). The XRD patterns after Three phases might exist in the uranium nitrides, UN, U_2N_3 and UN_2 . However, the other two phases are not detected herein owing to the proper U and N ratio and suitable growth condition. UN_2 phase with CaF_2 structure has very similar crystal structure to U_2N_3 phase and often difficult to distinguish from one another. However, the appearance of (321) and (411) diffraction peaks indicate the low symmetry of U_2N_3 with Mn_2O_3 structure. As shown in Fig.1 (a), the XRD peaks of U_2N_3 before sputtering are weakened and broaden, indicated the reduced grain size of uranium nitriding. After deposition, the U_2N_3 film is preferentially oriented along (400) plane, as seen from Fig.1 (b). AES depth profiles of uranium nitrides show that there is some inevitable natural oxidization on the surface of U_2N_3 . Nevertheless, after

minutes of sputtering, the oxygen concentration decreases to stable 3%, while the uranium concentration is about 39% and nitrogen is about 58% with a close atomic ratio of N/U consistent with the stoichiometric ratio of U_2N_3 .

Fig. 1. (a) XRD patterns of U_2N_3 from PDF card and before sputtering, (b) XRD patterns of U_2N_3 film, and the insert is AES depth profiles.

The SEM morphology of original uranium metal is shown in Fig.2 (a). The surface is very flat with coarse grains. The morphologies of the U_2N_3 sample are presented in Fig.2. The surface is quite flat and dense except for a small amount of cracks and holes that might be caused during the sputtering process, as shown in Fig. 2(b). TEM analysis is adopted to investigate the microstructure of the U_2N_3 phase as illustrated in Fig.2 (c) and it consists of polycrystalline with nanometer grain size of 10~50 nm. High resolution electron microscopy (HRTEM) observation of single grain as presented in the insert indicates the (222) lattice spacing of U_2N_3 phase.

Fig. 2. (a) SEM image of uranium metals before nitriding, (b) SEM image and (c) TEM image of U_2N_3 sample, and the insert in (c) is the HRTEM image of the U_2N_3 grain.

3.2 Thermoelectric properties

Fig.3 (a) shows electrical conductivity of U_2N_3 as a function of temperature. It is noted that U_2N_3 has quite good electrical conductivity with values as large as 302 S/cm at 243 K. The value decreases to 202 S/cm as the temperature increases to 383 K, indicating the semimetallic behavior of U_2N_3 .

The temperature dependence of the measured Seebeck coefficient is plotted in Fig. 3(b). The negative Seebeck coefficient of U_2N_3 suggests *n*-type conduction and the absolute value is 87 μ V/K at 243 K, increasing to 133 μ V/K at 383 K. The magnitude of Seebeck coefficient, corresponding to semimetallic behavior of U_2N_3 , is much larger than that of metals with values not larger than several μ V/K at room temperature [5]. The Seebeck coefficients of UB_4 and UN range from 0~40 μ V/K and 0~50 μ V/K given by Nishi et al [4] and Samsel-Czekala et al [10], respectively. As seen, the results of U_2N_3 are much higher than that for UB_4 and UN. The large absolute values of Seebeck coefficient indicate that the wave function of 5f electrons in U_2N_3 is widely expanded, resulting in strong scattering of conductive electrons by the 5f electrons near the Fermi level vicinity. In our future work, the electronic structures including the density of states and band structures of uranium nitrides will be further explored in depth.

Fig. 3. Temperature dependences of (a) electrical conductivity σ , (b) Seebeck coefficient α , and (c) power factor $\alpha^2\sigma$.

The power factor ($\alpha^2\sigma$) indicates the electrical output of thermoelectric materials. High electrical conductivity together with high Seebeck coefficient leads to favorable power factors as shown in Fig. 3(c).

The power factor of U_2N_3 increases monotonically with increasing temperature. The maximum Power factor is $3.58 \mu\text{Wcm}^{-1}\text{K}^{-2}$ obtained at 383 K. This value is one order of magnitude larger than that of uranium oxides and uranium borides, which is $0.13 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 300 K for UB_4 [4]. As compared with some state-of-the-art thermoelectric materials, the maximum power factor of the uranium nitride is also very favorable, close to the classical oxide thermoelectric material NaCo_2O_4 , which is $3.6 \mu\text{Wcm}^{-1}\text{K}^{-2}$ between 100 and 400 K [12]. Nevertheless, when compared to the most well-known Bi_2Te_3 based alloys (about $15 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 300 K) and PbTe based alloys (about $30 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 300 K) [13-15], the power factor of U_2N_3 still need to be further explored through the means of doping and alloying in our future work.

4. Conclusions

In summary, this study is primarily aimed at exploring new types of uranium nitrides thermoelectric materials. U_2N_3 sample fabricated by glow plasma nitriding consists of polycrystalline with nanometer grain size of 10~50 nm. It turns out that the values of electrical conductivity and the Seebeck coefficient of U_2N_3 are very considerable during 243 K to 383 K. The 5f electrons near the Fermi level that strongly scatter the conduction electrons are considered to be benefit for the improvement of Seebeck coefficient.

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