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Study on the electronic structure of α-U_2N_3 by XPS and first principles

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ABSTRACT

Film samples of α-U_2N_3 were prepared. The stoichiometry and crystal structure of the samples were identified to be α-U_2N_3 by AES and XRD separately. U 4f peaks in XPS spectra are obvious asymmetry, indicating that α-U_2N_3 has some metallic bonding character. The U 5f electrons are in localized state, which produces a strong and sharp peak near the Fermi level. The theoretical results from first principles calculations are in good agreement with the XPS data. Compared with UN, the valence charge of U atoms in α-U_2N_3 is higher, and the covalent property between U–N atoms is more evident. However, in XPS spectra no distinct shift of N 1s peaks is observed between the two nitrides.

1. Introduction

As potential fuels for next generation nuclear reactors, uranium nitrides have received much attention in years [1,2]. Compared to uranium oxides, which have been researched universally, there still are many problems in the present study of uranium nitrides [3,4]. Especially when uranium atoms bonding with nitrogen atoms, the 5f electrons of uranium exhibit some interesting properties, which have attracted attention among the research of heavy fermion systems [5]. In-depth study of the electronic structure of uranium nitrides is helpful to predict the behaviors of uranium nitrides during nuclear fuel cycle of storage, usage and disposal, and also better understand the influence of the 5f electrons on the properties of actinide compounds.

In recent years, there have been some reports on the characteristics of U–N bond from the perspective of organic chemistry [6–8], but the study of uranium nitrides is somewhat one-sided from the perspective of materials. There are many experimental and theoretical studies on UN, however, uranium nitrides with higher nitrogen content is lack of attention. Most researchers agree that there are three kinds of uranium nitrides in existence when atomic ratio of N/U larger than one [3,9], which are α-U_2N_3, β-U_2N_3 and UN_2, with crystal structure of Mn_2O_3-type, La_2O_3-type, and CaF_2-type, respectively. For β-U_2N_3 and UN_2, there are some theoretical researches by using the first principles method [10–12], but α-U_2N_3 has never been involved due to the large number of atoms in one unit cell. In addition, most researches on α-U_2N_3 are based on powder samples [13,14], which are difficult to obtain information of electronic structure.

Black [15] prepared thin films of uranium nitrides by sputtering method, and a series of studies on the electronic structure of uranium nitrides were made. The variation of U 4f XPS spectra with nitrogen content in the nitride films was measured. According to the XPS and UPS spectra obtained by Black, α-U_2N_3 is a kind of material that is proximity to ceramic. Some latter papers reported there are components proximity to metal presence in the nitrogen-rich uranium nitride films [16,17]. Our group also reported this phenomenon recently [18], but the essence of these components is not clear yet.

In comparison with UN_2, the existence of which still has argument [4,19], and β-U_2N_3, which only exists at high temperature, the α-U_2N_3 is a more common uranium nitride, but its electronic structure has not been clearly recognized. Here our group prepared α-U_2N_3 thin films, and analyzed the samples in various methods. With the help of first principles calculation, that was the first time carried out on α-U_2N_3, the electronic structure of α-U_2N_3 was researched.

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2. Experimental and computational methods

The film samples of uranium nitride were prepared by hollow cathode sputtering. To avoid forming UN_2 or non-stoichiometric U_2N_{3+x}, referring to Silva's data [14], the substrate temperature was controlled around 700 °C, to ensure the formation of stoichiometric α-U_2N_3. Base pressure of the vacuum chamber was 2×10^{-5} Pa. The sputtering gas was mixture of Ar and N_2, with flux ratio of 1:1. The purity of both gases was 99.999%, and the working pressure was about 6 Pa. The film was deposited on (100) oriented silicon wafers.

The elements concentration of the samples was investigated by AES depth profiles using a PHI650-SAM system. The cylindrical mirror analyzer (CMA) was adopted for measurements with the electron beam energy of 3 keV and current of 100 nA. During the depth profile process, the sputtering was carried out by an Ar ions gun with the energy of 4 keV and the spot size of about 1 mm^2. The crystal structure of the film samples was analyzed by XRD in θ-2θ geometry using an X'Pert PRO system with a Cu Kα radiation (λ = 1.5406 Å). The scanning range was 2θ = 25°–65°.The surface chemical states were investigated by an ESCALAB 250 system with a base pressure of 5×10^{-8} Pa. X-ray photoelectron spectroscopy (XPS) were taken using a mono-chromatized Al Kα radiation (1486.6 eV) and recorded by the hemispherical analyzer with a step-size of 0.05 eV.

First principles calculations were performed by using the Vienna ab initio simulations package (VASP) [20,21] with the projected-augmented-wave (PAW) pseudopotentials [22]. The exchange and correlation effects were described within GGA-PBE [23]. The electron wave function was expanded in plane waves up to a cutoff energy of 500 eV. We adopt the single unit cell to perform the electronic structure calculations. For the α-U_2N_3 unit cell containing 80 atoms, we used a Monkhorst–Pack [24] 3 × 3 × 3 mesh in Brillouin zone (BZ) integration, while for the UN unit cell containing 8 atoms, a 12 × 12 × 12 mesh was adopted, which were sufficient to get system energy converged to less than 1.0×10^{-4} eV. More details could be found in Ref. [11].

3. Results

The composition and structure of the film sample were analyzed firstly. Fig. 1 shows the AES depth profile of film. Some oxidations occur at the sample surface, in consistent with previous reports of uranium nitride [25,26]. After a few minutes sputtering, the atomic concentration of oxygen decreases to about 3%, and remains stable. While the nitrogen concentration increases to 58% and uranium is about 39%. The atomic ratio of N/U was about 1.48, which is close to the stoichiometric ratio of U_2N_3.

Fig. 2 is XRD pattern of the film. It can be seen that the film deposited on silicon wafers has a clear (400) preferred orientation due to the high substrate temperature. After taking logarithm to the altitude of the diffraction peaks, more diffraction peaks appear. The main diffraction peaks are in accordance with the characteristics of α-U_2N_3. The α-U_2N_3 with Mn_2O_3 structure and UN_2 with CaF_2 structure are very similar in crystal structure, and the main diffraction peaks of these two phases are close in the XRD spectra. Because of the low symmetry of Mn_2O_3 structure, more diffraction peaks would appear during XRD measurement [9]. In Fig. 2, the diffraction peaks of (411) and (611) indicate that the α-U_2N_3 phase which shares Mn_2O_3 structure exists in the film. Diffraction peaks near 32.8° (which is marked by a square symbol), belongs to the (200) planes of UO_2 impurity.

Based on the AES and XRD data, we successfully obtained α-U_2N_3 film samples containing a small amount of UO_2 impurity, which establish a basis for the study of the electronic structure of α-U_2N_3.

The electronic structure of the main elements in the film was analyzed by XPS. The thin oxide layer on the surface of the nitride was removed by Ar ions sputtering before analysis. When the oxygen concentration was low and kept stable, the XPS spectra of other main elements were recorded. Fig. 3 (a) (b) (c) are XPS spectrums of O 1s, C 1s, U 4f and N 1s respectively. The C 1s has no obvious intensity, indicating that there is no carbon impurity in the film. The intensity of O 1s peak at 530.9 eV is weak, which is similar with that of UO_2 [27]. This confirms previous estimation of the oxygen purity state.

Fig. 3(C) is XPS spectrum of U 4f and N 1s. It can be seen in the figure, the shape of U 4f peaks are obviously asymmetry, which indicates that there is a high density of states (DOS) at the Fermi level, and shows that this nitride has metallic properties. The peaks of U $4f_{7/2}$ and $4f_{5/2}$ are located at 377.8 eV and 388.6 eV separately, which are slightly higher than those of U 4f peaks of the uranium metal (376.8eV and 387.6eV), lower than those of uranium oxide

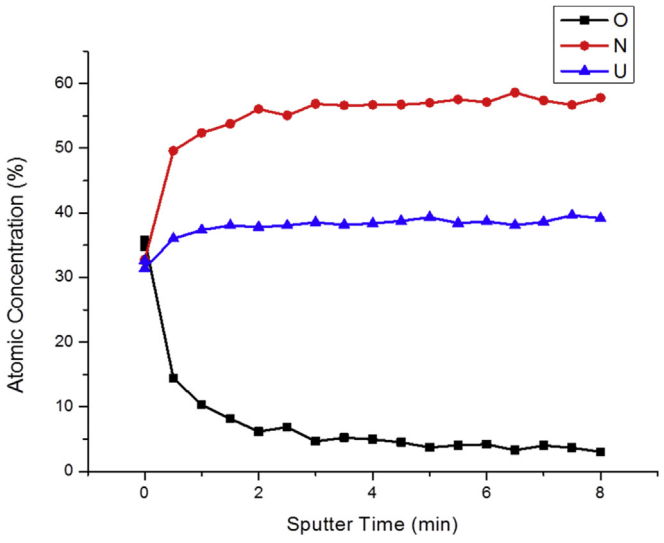

Fig. 1. AES depth profiles of main elements in the film sample.

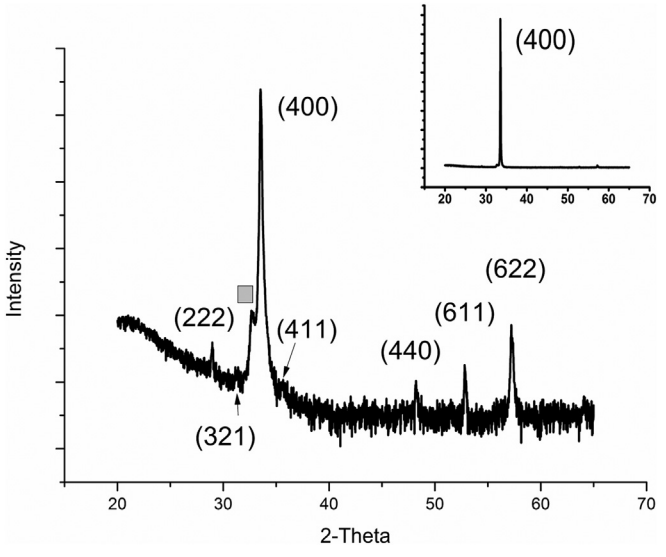

Fig. 2. XRD pattern of the film sample. The altitude of peaks has been taken logarithm, and the origin data is showed in the upper right corner.