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The crystal structure of high temperature phase Ta_2O_5

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Abstract

The high temperature phase of Ta_2O_5 and its variants were maintained in a pure Ta_2O_5 specimen using the conventional solid-state reaction method and the advanced laser irradiation technique. The structure of the high temperature phase is determined to be tetragonal with lattice parameters of $a = 3.86$ Å and $c = 36.18$ Å and space group of $I4_1/amd$. Compared to the previously reported crystal structure, the number of the total basis atoms was reduced to be 6 from 11. The modified crystal structure interprets well the recorded high-resolution electron microscopy images and the selected area electron diffraction patterns. Based on the basic tetragonal structure, the crystal lattice structures of the orthorhombic and monoclinic variants were determined and the corresponding space groups were analyzed according to the variation of the symmetrical elements. In addition, crystal atomic structures of these two variants were proposed based on the tetragonal structure.

Keywords: Crystal structure; High temperature phase of Ta_2O_5 (H-Ta_2O_5); High-resolution electron microscopy (HREM); Simulation

1. Introduction

The research conducted in the fields of materials science and modern physics related to microelectronics industry is mostly driven by the demand for smaller components with enhanced performance. For micro- or even nanocapacitors, which form the basis of many memory devices, the dielectric constant limits the degree of miniaturization – a limit that is now being approached for the materials currently in use. For this reason, some exotic compounds with high dielectric constants are being investigated. Ta_2O_5 is considered to be one of the promising candidates. To improve the dielectric properties, TiO_2, SiO_2, Al_2O_3 and ZrO_2 were doped in Ta_2O_5 [1–4]. Though all of these doping systems showed improvement, only the dielectric constant of the Ta_2O_5–TiO_2 system was greatly enhanced. The enhancement of dielectricity with doping TiO_2 was thought to be through the low temperature Ta_2O_5 (L-Ta_2O_5) phase transforming to the high temperature phase (H-Ta_2O_5). Some subsequent extensive research about the Raman spectrum was conducted to try to understand the doping effects of the Ta_2O_5–TiO_2 system [5,6]. However, because of uncertainty about the crystal structure of H-Ta_2O_5, great challenges exist in determining the vibration modes of the Ta_2O_5–TiO_2 system. Determination of the crystal structure of H-Ta_2O_5 has become critical, and would greatly help the understanding of the physical mechanisms of the huge enhancement of dielectric permittivity in the Ta_2O_5–8%TiO_2 system. It may also help in understanding the universal doping effects in other systems.

Extensive research has been conducted to try to decode the crystal structure of H-Ta_2O_5. Lagergren in 1953 reported an orthorhombic unit cell with $a = 35.6$ Å, $b = 3.79$ Å and $c = 3.735$ Å [7]. Later Zaslavskii concluded that the high temperature form was tetragonal with $a = 3.801$ Å and $c = 35.67$ Å [8]. In 1964, Laves and Petter isolated three polymorphic forms: (i) two monoclinic structures, the first one with $a = 3.784$ Å, $b = 3.802$ Å,

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$c = 35.82$ Å and $\beta = 91°$ and the second with $a = 5.365$ Å, $b = 5.365$ Å, $c = 35.85$ Å and $\beta = 91°$; (ii) a tetragonal structure with $a = 3.795$ Å and $c = 35.54$ Å [9]. In 1968, Waring and Roth systematically studied the effect of TiO_2 doping on the polymorphism of tantalum pentoxide (Ta_2O_5–TiO_2 system). They reported three types of lattice structure of H-Ta_2O_5: (i) tetragonal: $a = 3.81$ Å and $c = 36.09$ Å; (ii) monoclinic: $a = 5.367$ Å, $b = 5.368$ Å, $c = 35.707$ Å and $\beta = 91°42'$ and $a = 3.794$ Å, $b = 3.807$ Å, $c = 35.70$ Å and $\beta = 90°51'$; and (iii) triclinic: $a = 3.794$ Å, $b = 3.807$ Å, $c = 35.70$ Å, $\alpha = 90°54.4'$, $\beta = 90°11.5'$ and $\gamma = 89°59.9'$ [10]. Because the high quality single crystal of H-Ta_2O_5 is very difficult to grow from pure materials, it has been always very difficult to decode the crystal structure of H-Ta_2O_5. Later, in 1971, Stephenson and Roth [11] stabilized the structure of H-Ta_2O_5 by doping Sc_2O_3 with 2 mol.% and obtained the single crystal H-Ta_2O_5–Sc_2O_3. From the investigation of this crystal, the crystal structure of H-Ta_2O_5 was proposed (the S-R model). They determined the space group of H-Ta_2O_5 to have an unpopular form of face-centered monoclinic C2 ($a = 35.966$ Å, $b = 3.810$ Å, $c = 3.810$ Å, $\beta = 96°7'$) and gave up the structure of body-centered tetragonal $I4_1/amd$. However, the crystal structure of pure H-Ta_2O_5 has never been reported and is always in dispute. In this study, we used the advanced laser irradiation technique and successfully reserved H-Ta_2O_5 at room temperature. This enabled us to use transmission electron microscopy (TEM) to decode the crystal structure of pure H-Ta_2O_5.

2. Experimental procedures

The pure Ta_2O_5 specimens were sintered using the conventional solid-state reaction technique with a mixture of pure Ta_2O_5 powder, then laser-irradiated using a laser-irradiation system with a cw CO_2 laser source. The details can be seen in Ref. [12]. The samples were cut into small plates of 3 mm diameter and 0.5 mm thickness. To prepare the TEM foils, these plates were mechanically polished to 60 μm thickness and then ion-milled. The TEM observations were carried out with a JEOL 2010 microscope. The high-resolution electron microscopy (HREM) experiments were conducted using a Field Emission Gun (FEG) JEOL 2010F microscope with a point resolution of 0.19 nm. The atomic model is set up with the commercialized software CrystalKit and the HREM simulation was carried out with Mactempas. The multi-slice approximation method was used in simulating the HREM images. The simulation parameters were chosen to be close to the experimental ones.

3. Results and discussion

3.1. The lattice structure and space group of H-Ta_2O_5

The laser irradiation of the sintered specimen allowed the high temperature phase structures of Ta_2O_5 to be kept at room temperature due to the extremely high cooling rate. A specimen with the H-Ta_2O_5 crystalline structure was obtained and first studied by the traditional selected area electron diffraction (SAED) technique. By systematically tilting the Ta_2O_5 TEM specimen, a series of selected area electron diffraction patterns (SAEDPs) of one kind of H-Ta_2O_5 phase were obtained. Fig. 1 shows the series SAEDPs taken from the H-Ta_2O_5 specimen. The reflection conditions are summarized in Table 1. The reflections can be indexed according to a body-centered tetragonal structure with lattice parameters of $a = 3.86$ Å and $c = 36.18$ Å. The zone axis of each diffraction pattern is shown in each figure. The experimental angles between the neighboring SAED patterns are shown in Fig. 1. Fig. 2 schematically illustrates the lattice structure of H-Ta_2O_5 in reciprocal space with $2 \times 2 \times 4$ unit cells. One unit cell is highlighted by black bold lines. Based on the reconstructed model, the angles between zone axes are calculated and shown in Table 2. The table reveals that the experimental values are in good agreement with the calculated ones. On the basis of the results of the crystal lattice structure obtained by the series electron diffraction, the space group of the high temperature phase of Ta_2O_5 can be determined by the reflection conditions of the SAEDP results. According to the International Tables for Crystallography [13] and the reflection conditions in Table 1, the space group of H-Ta_2O_5 is uniquely determined as $I4_1/amd$ (No. 141). Following is a general description to determine the space group based on the extinction rules of the reflection condition in the series selected area diffraction patterns. First, the general reflection condition $h + k + l = 2n$ indicates that the H-Ta_2O_5 structure is a body-centered tetragonal one. Second, the reflection conditions of $00l$ reflections is $l = 4n$, which means that this tetragonal structure includes a 4_1 screw axis along the [0 0 1] direction and the reflection conditions of $hk0$ reflections ($h, k = 2n$) indicates the existence of "a" and "b" glide planes perpendicular to the c-axis. The possible space groups which agree with the above reflection conditions are $I4_1/a$, $I4_1/amd$ and $I4_1/acd$. Finally, the reflection conditions of $0kl$ reflections ($k + l = 2n$) and hhl reflections ($2h + l = 4n$) exclude the space group $I4_1/acd$ and $I4_1/a$, respectively. Thus the uniquely determined space group of this tetragonal structure is $I4_1/amd$.

3.2. HREM images and simulations

The atomic structure of the H-Ta_2O_5 phase was decoded by HREM images and the corresponding simulations. Fig. 3a and b are the structural HREM images taken along the zone axes of $[0\bar{1}0]$ and $[1\bar{1}0]$, respectively. The bright dots can be regarded as the projections of Ta atomic columns and the dark regions as channels among atoms. A three-layer periodicity is denoted with bold white arrows in Fig. 3b. This characterization is an indicator of the 4_1 screw axis in the crystal structure of H-Ta_2O_5. The insets in Fig. 3 are the simulated HREM images according