Growth and dielectric properties of Ta_2O_5 single crystals grown by laser heated pedestal growth technique

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Abstract Ta_2O_5 single crystals have been grown by the laser heated pedestal growth (LHPG) technique up to several centimeters length with diameter of 1.1 mm. The crystal, characterized by X-ray diffraction, dielectric measurement, and thermal expansion analysis, has H_{tri}-Ta_2O_5 symmetry. Dielectric permittivity, loss tangent along [001] and [110] direction were investigated over the temperature range from −180 °C to 100 °C. Large dielectric anisotropy in Ta_2O_5 single crystal was observed. At room temperature, the dielectric permittivities (1 MHz) along [001] and [110] are 33.2 and 231.9, respectively. The reason of dielectric enhancement in Ta_2O_5 crystal grown by LHPG was also discussed.

Key words materials; laser heated pedestal growth (LHPG); single crystals; Ta_2O_5; dielectric properties.

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1. Introduction

New capacitor materials with high dielectric constant and low leakage are required for advanced dynamic random access memory (DRAM) cells to keep up with the scaling rule of present-days microelectronic and microwave communication technologies. Among these, Ta_2O_5 has emerged as the most promising candidate as it is compatible with microelectronics manufacturing and forms good quality films under microelectronics-compatible processing condition[1~3]. There has been a lot of research on the ceramic processing[4] and film deposition of Ta_2O_5[5,6]. However, before Ta_2O_5 can be successfully utilized for device integration, its material properties need to be better understood. It is envisaged that in Ta_2O_5 crystal, because of anisotropy of physical properties, the dielectric permittivity may be larger in some crystalline directions than those in ceramics. However, to our knowledge, there have been few reports so far on the methods of growing Ta_2O_5 crystals and on the dielectric properties of Ta_2O_5 single crystal with respect to its crystalline orientations, because of the high melting temperature of Ta_2O_5 around 1900 °C.

The laser heated pedestal growth (LHPG) technique is a powerful tool for rapid growth of small diameter single crystals for both property study and fiber devices[7,8]. The LHPG technique has several unique features that are special important for growing Ta_2O_5 crystals. The advantages include containerless crystal growth, capability of growing high melting temperature oxides, rapid growth rate, and ease of controlling growth temperature, rate, and orientation to reach good crystal quality.

In this paper, we report the growth of Ta_2O_5 single crystal fibers using LHPG technique. The dielectric and thermal expansion properties of the grown crystals are studied over a wide temperature range. The reason of dielectric enhancement in crystals grown by LHPG technique is also discussed.

2. Experiment

The LHPG equipment consisted of a CO_2 power source (180 W), an optical layout, and a growth section. An optical pyrometer was used to monitor the shape of the molten zone during growth and to measure the molten zone temperature of the composition. The source rods for LHPG were prepared by a conventional solid state reaction method using reagent grade Ta_2O_5 (*Alfa AESAS* Puratronic). A circular pellet of Ta_2O_5 was pressed and sintered at 1600 °C in the air for 4 hours. The fired ceramic pellet was cut into ∼ 1.2 × 1.2 (mm) rods approximately 30 mm in length as feed rods for the crystal growth.

Dielectric permittivity and loss tangent as functions of temperature (−180 ∼ 100 °C) at discrete frequencies (from 1 kHz to 1 MHz) were measured by using an automated dielectric setup equipped with a HP4284A LCR meter. To ensure good comparability, all samples are annealed in the air at 550 °C for 5 hours prior to sputtering gold electrodes onto the surfaces for the electrical measurement. A high precision General Radio 1621 capacitance system was also used to corroborate the dielectric properties at room temperature particularly for small single crystal samples to enhance accuracy and precision. All the measurements upon temperature were performed in cooling runs with cooling rate around 2 °C/min.

Thermal expansion measurements were carried out from −160 °C to 600 °C using a high-sensitivity linear voltage differential transformer dilatometer (Dilatronic

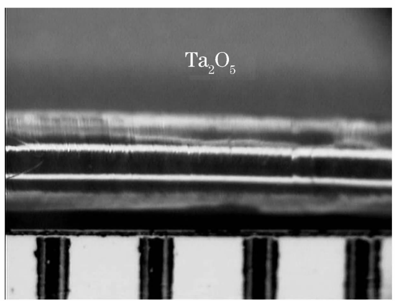

Fig. 1. Photograph of Ta_2O_5 single crystal grown by the LHPG technique. Each division equals 1 mm.

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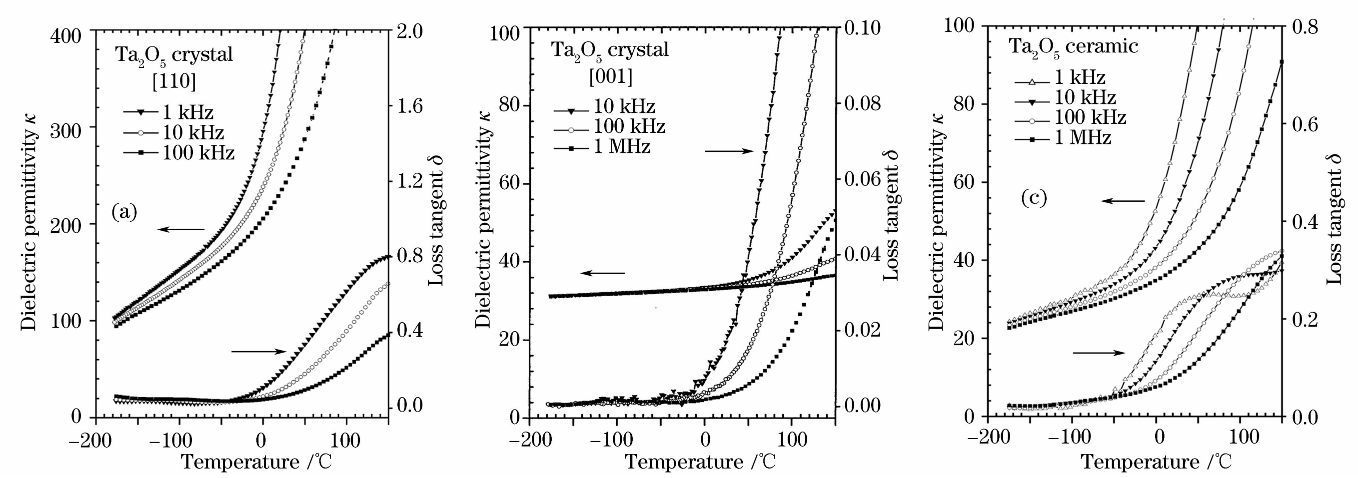

Fig. 2. Temperature and frequency dependence of the dielectric permittivity and loss tangent for (a) LHPG grown Ta_2O_5 single crystals along the [110] direction; (b) LHPG grown Ta_2O_5 single crystals along the [001] direction; (c) Ta_2O_5 ceramics.

VIII, Theta Industries, Inc.). Expansion measurements were regulated at 2 °C/min for both heating and cooling runs.

3. Result and discussion

With careful alignment of the feed rod and precise control of the shape and temperature of the molten zone, single crystals of Ta_2O_5 were grown successfully using the LHPG technique. Both the feeding rods and the pulling seeds were Ta_2O_5 ceramics. All growths were performed in the air, with pulling speed of 25 ∼ 30 mm/h. The stable molten zone temperature was 2020 °C, with an estimated accuracy of ±30 °C. Figure 1 shows the typical LHPG grown Ta_2O_5 crystal fiber, 25 mm in length and 1.1 mm in diameter. The crystals were transparent and colorless and most of them were free of cracks. Inclusions and coring were not observed. Diameter variation was less than 2%. Optical observations show the two clear facets on opposite sides of the fiber, running along the length of the fiber. Parallel to the facets, the crystal fiber can be cleaved along the growth direction with the (001) surface, which is confirmed by the X-ray single crystal diffraction. The crystal fiber growth direction was found to be along [110] determined by Laue back-reflection photography. Powder X-ray diffraction for the as-grown crystal revealed that the crystal contains H_{tri}-Ta_2O_5 phase and has triclinic symmetry[9].

Dielectric permittivity and loss tangent as functions of temperature (−180 ∼ 150 °C) and frequency (1 kHz∼1 MHz) are measured on LHPG grown Ta_2O_5 single crystal samples along the [110], [−110] and [001] directions, respectively, as shown in Figs. 2(a) and (b). For comparison, the dielectric properties of Ta_2O_5 ceramics are also presented in Fig. 2(c).

The dielectric data at 20 °C for the 1 MHz measurement and temperature coefficient of dielectric permittivity (Q_κ) in the −20 ∼ 60 °C temperature interval are list in Table 1.

In Fig. 2, the dielectric permittivity is quite large for Ta_2O_5 crystal along [110] direction over the entire range of variables. At 20 °C and 1 MHz, the dielectric permittivity is 231.9, which is about 6.2 times than that of Ta_2O_5 ceramics. As the temperature increased, the

Table 1. Dielectric Properties of Ta_2O_5 Crystal and Ceramic Measured at 1 MHz

Species	κ (20 °C)	$\tan\delta$ (20 °C)	Q_κ (ppm/K) (−20 ∼ 60 °C)
Ta_2O_5 crystal [110]	231.9	0.0604	6867
Ta_2O_5 crystal [−110]	230.6	0.0601	6849
Ta_2O_5 crystal [001]	33.15	0.0028	453
Ta_2O_5 ceramic	37.52	0.0789	5267

dielectric permittivity rises and becomes increasingly more frequency dependent. The Ta_2O_5 crystal samples along [110] direction exhibit a dielectric behavior similar to glasses, where it is believed that the behavior is the result of mobile ions (cations) moving through the open structure of glass. Similar results were also obtained from the crystal samples along [−110] direction.

Unlike the behavior of Ta_2O_5 crystal samples along [110] and [−110] directions, the dielectric permittivity of Ta_2O_5 crystal samples along [001] direction exhibits smooth and frequency independent curves below 20 °C as shown in Fig. 2(b). At 20 °C and 1 MHz, the dielectric permittivity and loss tangent are 33.15 and 0.0028, respectively. Both are low in comparison with the ceramic results.

It is noted that (i) large dielectric anisotropy exists in Ta_2O_5 crystal, which is related to the anisotropy of crystal structure; (ii) The average value of the dielectric permittivity of Ta_2O_5 crystals grown by LHPG technique is 4 times more than that of Ta_2O_5 ceramics, which means the phase of Ta_2O_5 crystal is different from that of Ta_2O_5 ceramic.

The polymorphism of Ta_2O_5 were extensively studied and there exist is a low temperature form β-Ta_2O_5 (L-Ta_2O_5) and a high temperature form α-Ta_2O_5 (H-Ta_2O_5)[9]. It was observed that the transformation of the β phase into the α one begins at about 1360 °C. The reverse transformation takes place slowly enough. If a sample of Ta_2O_5 ceramic is sintered at a temperature above 1360 °C and then is cooled to room temperature slowly, the main phase of the ceramic is β-Ta_2O_5.

The high temperature form of Ta_2O_5 was found to have a number of metastable phases indicated as H_{tri}-

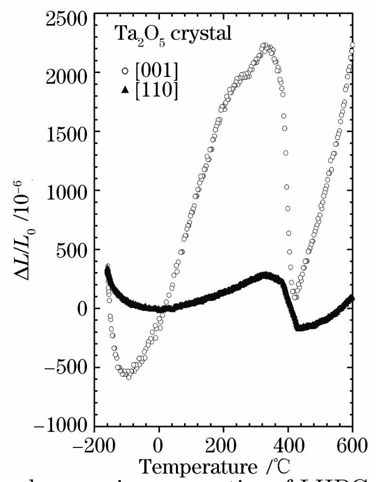

Fig. 3. Thermal expansion properties of LHPG grown Ta_2O_5 single crystals along the [001] and [110] directions.

Ta_2O_5, H_{mon}-Ta_2O_5, and H_{tet}-Ta_2O_5. When quenched from above the stable 1360 °C to room temperature Ta_2O_5 has undergone at least two metastable phases (tetragonal→monoclinic→triclinic)[9]. Because of this, attempts to grow crystals of Ta_2O_5 by the LHPG method result in the production of crystals of H_{tri}-Ta_2O_5 and not β-Ta_2O_5. It is concluded that Ta_2O_5 with H_{tri}-Ta_2O_5 structure has large dielectric permittivity.

It was found that the triclinic form of Ta_2O_5 undergoes a phase transition on heating at about 320 °C to a monoclinic modification (H_{mon}-Ta_2O_5)[9]. Figure 3 shows the thermal expansion of Ta_2O_5 single crystals with variation of temperature both along [110] and [001] directions. There is a discontinuous change of thermal strain between 360 °C and 380 °C for the Ta_2O_5 single crystals, which indicates the phase transition from H_{mon}-Ta_2O_5 to H_{tri}-Ta_2O_5.

4. Conclusions

Single crystals of Ta_2O_5 have been grown successfully using the LHPG technique. The as-grown crystal, characterized by X-ray diffraction, dielectric measurement and thermal expansion analysis, has H_{tri}-Ta_2O_5 symmetry. High dielectric permittivity and large dielectric anisotropy of Ta_2O_5 single crystal were measured, which is of special significance in low-dimensional microelectronic devices. The LHPG technique has been demonstrated to be useful in the crystal growth of a high temperature form system.

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