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# A Phototropic Crystal Growth of $\beta$-$Ta_2O_5$ by KrF Laser Photolysis of $Ta(OCH_3)_5$

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Sublimated $Ta(OCH_3)_5$ gas was decomposed by KrF excimer laser under the coexistence of helium gas. The deposit obtained was strongly-oriented $\beta$-$Ta_2O_5$, which had columnar structure. It grew nearly toward the irradiation direction of the laser light.

In recent years, considerable interest has grown in developing photo CVD methods for synthesizing thin films owing to its advantage as a method of producing uniform films with desired properties. UV light irradiation is considered to promote the migration of adsorbates on the substrate surface and improve the surface morphology.[1,2] In parallel with studies of photo CVD process of oxide ceramics such as $Al_2O_3$,[3] $SiO_2$,[4,5] etc., those of tantalum oxide films have attracted much interest for their use as a storage capacitor in very large scale integrated circuit (VLSI) because of its higher dielectric constant. Tantalum oxide is also useful for protective coating against a highly corrosive environment encountered in the process of alternative energy production, such as thermochemical hydrogen production from water, because of its superior chemical stability.

The film formation of tantalum oxide by several different techniques has been investigated.[6-9] All the deposited films were amorphous except for those obtained by high-temperature thermal CVD[6] or by sputtering at substrate temperatures above 570 K.[8] Yamagishi and Tarui succeeded in preparing Ta-O film[9] by photolysis of $Ta(OCH_3)_5$ using a low pressure mercury lamp, but the reported structure was amorphous.

In the present study, we obtained a strongly-oriented tantalum oxide film by photolysis of $Ta(OCH_3)_5$ under the KrF laser irradiation.

Experimental setup for laser CVD is composed of (1)a deposition chamber of stainless steel connected to a vacuum system, and (2)a vaporizer of $Ta(OCH_3)_5$. The vaporizer was maitained at 383 K to sublimate $Ta(OCH_3)_5$. The sublimated gas was flowed into the deposition chamber with a flow of helium gas (100 $cm^3$ $min^{-1}$). The deposition chamber, equipped with a synthetic quartz window, was heated to 403 K to prevent the condensation of $Ta(OCH_3)_5$. Helium was also introduced to the inside of the window at the flow rate of 50 $cm^3$ $min^{-1}$ in order to prevent the sublimated gas from depositing on the window. The total pressure was maitained constant at 1.00 Torr by a vacuum valve placed between the deposition chamber and the vacuum system. Supply rate of $Ta(OCH_3)_5$ into the chamber was monitored by load-cell weighing to be 200 mg $h^{-1}$.

The unfocused beam of KrF laser (Lumonics Model HE-460-SM-A) was irradiated through a synthetic quartz window at the repetition rate of 50 Hz. The cross section of the beam passing through the exit aperture of the laser was 1.0 $cm^2$ (0.5 X 2.0 cm). The laser fluence was adjusted to 45 mJ $cm^{-2}$. A quartz glass substrate was heated to the same temperature as that of the surrounding deposition chamber to prevent $Ta(OCH_3)_5$ vapor from condensing onto it. Black films were obtained at the spot of laser irradiation, whereas no deposits by thermal decomposition of $Ta(OCH_3)_5$ were found on the substrate without laser irradiation.

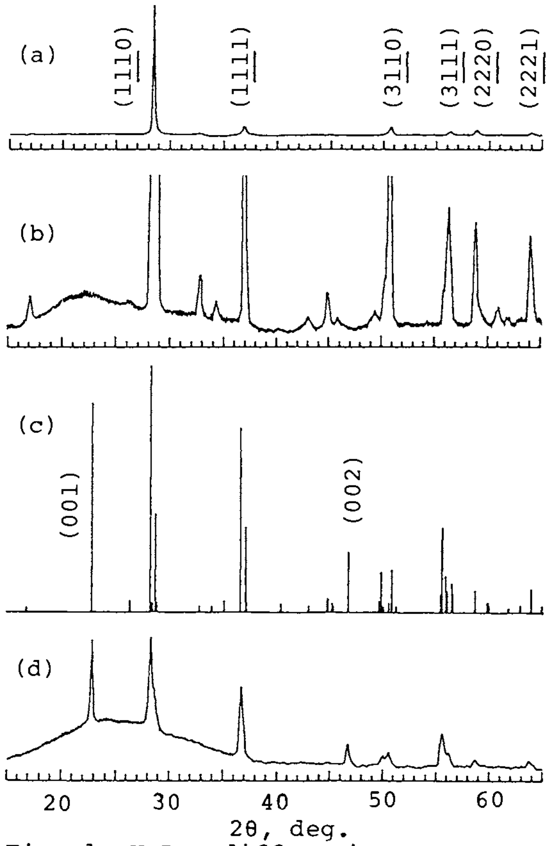


Fig. 1. X-Ray diffraction pattern of deposit and the data from JCPDS diffraction file.
(a) as-deposited film,
(b) same as (a), by an increased sensitivity,
(c) standard powder pattern of $\beta$-$Ta_2O_5$ (JCPDS 25-922),
(d) pulverized mixture of deposited film and substrate.

An example of CuK X-ray diffraction (XRD) pattern of the deposits obtained by laser irradiation is given in Figs. 1(a) and (b), where the incident angle of laser beam to the substrate was 60°. Though not so many numbers of diffraction peaks were observed by smaller sensitivity, an increase in sensitivity factor by a factor of 30 enabled us to find other satellite peaks, as shown in Fig. 1(b). Presence of these satellite peaks seems to indicate that the deposit is orthorhombic $\beta$-$Ta_2O_5$ (JCPDS 25-922), represented by Fig. 1(c), and not hexagonal $\delta$-(Ta-O) (JCPDS 19-1299). The intense diffraction peaks in Fig. 1(a) correspond to the diffraction from the following planes of $\beta$-$Ta_2O_5$ ; (1 11 0), (1 11 1), (3 11 0), (3 11 1), (2 22 0), and (2 22 1).

Intense diffraction peaks indexed above and the lack of diffraction from (0 0 1) and (0 0 2) planes imply that the deposited film has a strong preferential orientation. To confirm this, the deposit was pulverized together with the substrate and its XRD pattern was examined. The result given in Fig. 1(d) clearly shows the presence of the diffraction peaks from (0 0 1) and (0 0 2) planes, as is expected.

In order to know the correlation between the preferred orientation of crystal growth and the direction of incident laser light, deposition experiments under different incident angles of laser light were conducted. The substrates were placed in the deposition chamber at angles of 30°, 60°, and 90° to the incident laser beam. The estimated deposition rates of films were 26, 54, and 67 nm $min^{-1}$

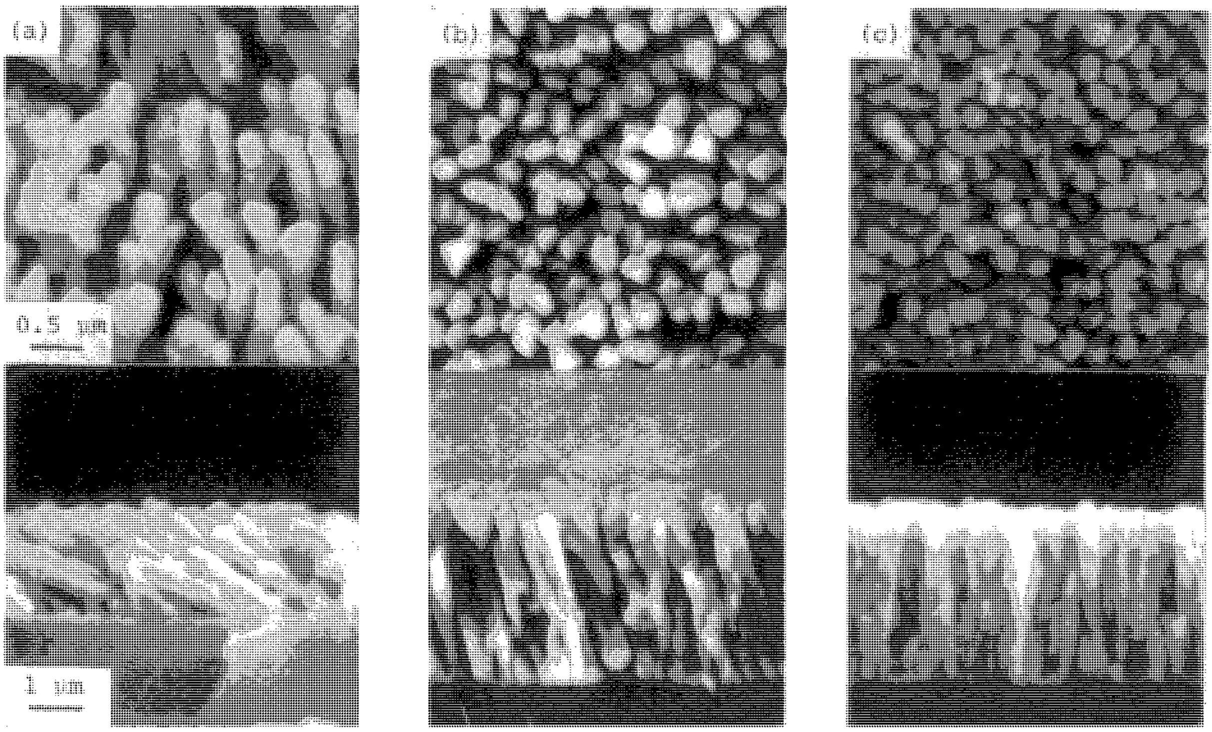


Fig. 2. Scanning electron micrographs of deposited film obtained by different irradiation angles to the substrate.
upper : surface, lower : cross section
Irradiation angle in each photo is 30° in (a), 60° in (b), and 90° in (c), respectively.

at the laser incident angles of 30°, 60°, and 90°, respectively. Both the surface appearance and the cross section of deposits observed with a scanning electron microscope (SEM) are given in Fig. 2. Columnar crystal growth is observed, the direction of which is dependent on the incident angle of laser beam. Though the direction of crystal growth does not strictly agree to that of incident light, there exists some correlation between these directions; $\beta$-$Ta_2O_5$ grows phototropically in KrF laser CVD process.

This phototropic crystal growth seems to be a characteristic of photodeposition by the powerful UV light irradiation under such conditions as mentioned above. In case of the irradiation condition of lower laser fluence (e.g. 20 mJ $cm^{-2}$), however, deposits showed only quite weak XRD peaks with a broad halo-pattern between ca. 15-40°(CuK$\alpha$) and the columnar structure was not found by SEM observation.

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