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Morphology and structure of tantalum oxide deposit prepared by KrF excimer laser CVD

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Tantalum oxide films have been deposited on substrates by decomposing $Ta(OCH_3)_5$ photolytically in the beam of a KrF excimer laser under various conditions of laser fluence (200–450 J m^{-2}), repetition rate (20–120 Hz), supply rate of $Ta(OCH_3)_5$ (50–400 mg h^{-1}) and substrate temperature (403–723 K). The deposits were highly oriented when produced at laser fluences of 350 and 450 J m^{-2}. Their XRD patterns suggested the formation of β-Ta_2O_5. The (1 1 1 0) planes were preferentially oriented parallel to the substrate surface when produced at lower repetition rates, higher supply rates of $Ta(OCH_3)_5$, and lower substrate temperatures; whereas (1 1 1 1) planes were similarly oriented when the conditions were reversed. The preferred orientation may be explained in terms of supersaturation. The deposits produced at a fluence of 200 J m^{-2} were, however, rather amorphous.

1. Introduction

The preparation of a very thin uniform film of tantalum pentoxide (Ta_2O_5) on a substrate has been intensively studied because of the potential for industrial application [1–6] of the film. Of the various techniques so far tried [1–5, 7–14] for the preparation, the high-temperature chemical vapour deposition (CVD) technique [8–10] is currently considered to be advantageous for bringing about a better step-coverage over a rough surface at a higher deposition rate. However, it has the disadvantage of requiring higher reaction temperatures (> 600 K), even if organometallic compounds, which are more readily decomposable than the corresponding halides, are used as the starting materials. Therefore, in the hope of facilitating the deposition reaction at lower temperatures and hence the formation of flawless deposits, research has recently been conducted on CVD reactions under the influence of radiation from a proper source, namely, photo-CVD reactions. Such studies have been reported by Tarui *et al.*, who worked with tantalum compounds, employing radiation from a low-pressure mercury lamp [15, 16].

We have also studied the formation of tantalum oxide deposit from tantalum pentamethoxide, $Ta(OCH_3)_5$, vapour under the influence of a KrF excimer laser beam. In the course of the work, a phototropic growth of highly-oriented oxide deposit was observed; and X-ray diffraction analysis suggested the formation of β-Ta_2O_5 [17]. Hence, further study was conducted on the effects that various deposition conditions would produce on the crystalline forms and the rate of deposition of tantalum oxide. The results of this latter study are described in this paper.

2. Experimental procedure

The same laser-CVD apparatus as described briefly in a previous paper [17] was used in this study. The arrangement of the individual units is schematically shown in Fig. 1. The principal part comprised a vertical cylindrical deposition chamber made of stainless steel, a vaporizer and a laser unit (Lumonics HE-460-SM-A, which is not shown in the figure). The deposition chamber, incorporating a substrate holder, had a horizontally projecting tubular passage for the incident laser beam, a feed-inlet and an outlet for connection with the vacuum system. The laser-beam passage had a synthetic-quartz window at the end opposite to the chamber and a purge-gas inlet branching out from the close vicinity of the window.

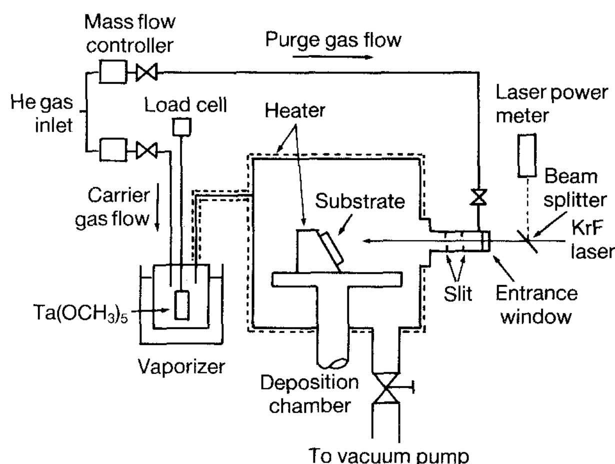

Figure 1 Schematic representation of the apparatus used for laser CVD experiments.

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Moreover, the passage was compartmented by a few slotted plates so as to assure the prevention of back-mixing.

The body of the chamber and the feed-inlet were kept at a temperature higher by 20 K than the temperature of the vaporizer so that the chance of the pentamethoxide vapour condensing in these parts might be removed. On the other hand, the laser-beam passage was kept at room temperature so as to prevent the gas mixture in the chamber from reaching the window.

Helium gas was used as the carrier of the pentamethoxide vapour from the vaporizer to the chamber and also as the purge gas. The carrier gas was supplied to the vaporizer at a rate of $100 \text{ cm}^3\text{min}^{-1}$ and the purge gas supplied to the laser-beam passage at a rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The total pressure in the chamber was maintained at 1.333×10^2 Pa by manipulating the outlet valve between the chamber and the vacuum system.

The rate of supply of the pentamethoxide was monitored by load-cell weighing and adjusted to $50–400 \text{ mg h}^{-1}$ by changing the vaporizer temperature within the limits 383 and 413 K. Depending upon the above rate of supply, the partial pressure of tantalum pentamethoxide in the deposition chamber was estimated to vary from 5.333×10^{-2} to 4.266×10^{-1} Pa.

The substrate was made of quartz and so placed in the deposition chamber as to be irradiated by the laser beam (unfocused) at an incident angle of 60°. The repetition rate was varied between 20 and 120 Hz and the laser fluence, monitored by a power meter (Scientech 38-2UV5), was adjusted to $200–450 \text{ J m}^{-2}$. The substrate temperature was varied in the range 403 to 723 K by a heater placed under the substrate.

The deposit formed was characterized by X-ray diffraction (XRD) and the crystal orientation determined by the same method. The microstructure was studied by a scanning electron microscope. The deposit thickness was determined from the difference between the measurements made of the substrate weight before and after deposition, by assuming that the density of the deposit was equal to that of Ta_2O_5 ($\rho = 8.73 \text{ g cm}^{-3}$).

The deposition conditions are summarized in Table I. Usually, no fewer than 1×10^5 laser shots were necessary to obtain an amount of deposit sufficiently great enough for characterization and determination of crystal orientation by XRD.

TABLE I Deposition conditions for laser CVD

Source material	$Ta(OCH_3)_5$
Supply rate of $Ta(OCH_3)_5$	$50–400 \text{ mg h}^{-1}$
Carrier gas	He
Wavelength of laser	248 nm(KrF laser)
Laser fluence	$200–450 \text{ J m}^{-2}$
Repetition rate	20–120 Hz
Substrate	Quartz plate
Substrate temperature	403–723 K
Chamber temperature	403 K
Total pressure in the chamber	1.333×10^2 Pa

3. Results and discussion

3.1. Crystallinity and deposition rate—their dependence on laser fluence

The oxide films produced under any set of experimental conditions were semi-transparent and ranged in colour from brown to blue-black or black. The elemental analyses and the chemical shift of Ta 4f core electron levels, which was measured by X-ray photoelectron spectroscopy, suggested that the deposits were non-stoichiometric oxides. Within the limits of experimental error, the deposits were found to contain scarcely any carbon.

Fig. 2 shows the effect that the laser fluence had on the deposition rate under conditions where the repetition rate, the rate of supply of the pentamethoxide and the substrate temperature were, respectively, 50 Hz, 200 mg h^{-1} and 403 K. The deposition rate increased approximately in proportion to the third power of the fluence.

The X-ray diffraction (XRD) patterns (CuK_α) of the deposits are shown in Fig. 3. Evidently, the deposits produced at a high fluence (450 J m^{-2}; Fig. 3a) were better crystallized, whereas the deposits produced at a low fluence (200 J m^{-2}; Fig. 3b) were poorly crystallized or rather amorphous. The XRD patterns of the former deposits were found to correspond to the pattern of β-Ta_2O_5, although certain of the known peaks were missing because of the strongly-preferred orientation of crystallites. Such was also the case with the deposit formed at a fluence of 350 J m^{-2}. Since the tantalum oxide films produced by earlier workers, excepting those prepared by high-temperature CVD and by sputtering at substrate temperatures above 570 K, are known to be amorphous and since the oxide deposits produced by CVD under the influence of the ray from a low-pressure mercury lamp or from a KrF laser at a low fluence were amorphous or exhibited quite weak XRD intensities, the crystallization of tantalum oxide and the growth of the crystals, both observed in this work, seem to be characteristic of the deposition effected by powerful u.v. light irradiation.

The surface and cross-sectional appearence are shown in Fig. 4. Laser irradiation at a high fluence resulted in columnar crystal growth, the direction of which was nearly parallel to that of the incident laser beam (Fig. 4a). On the other hand, irradiation at a low fluence resulted in the formation of a dense and homogeneous deposit exhibiting no particular direction of crystal growth (Fig. 4b).

3.2. Crystal orientation and its dependence on some variables

Since, as noted above, the XRD spectra in Fig. 3a suggested the preferred orientation of crystallites and since the orientation was suspected to depend on some variables, the preferred orientation was studied, by making use of Lotgering's orientation factor [18], as a

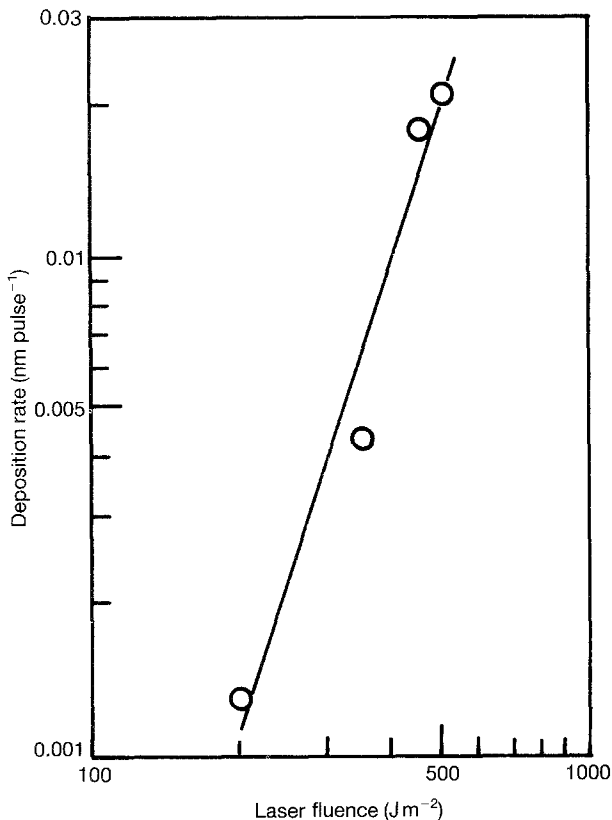

Figure 2 Dependence of deposition rate on laser fluence. (Repetition rate, 50 Hz; substrate temperature, 403 K; supply rate of $Ta(OCH_3)_5$, 200 mg h^{-1}.)

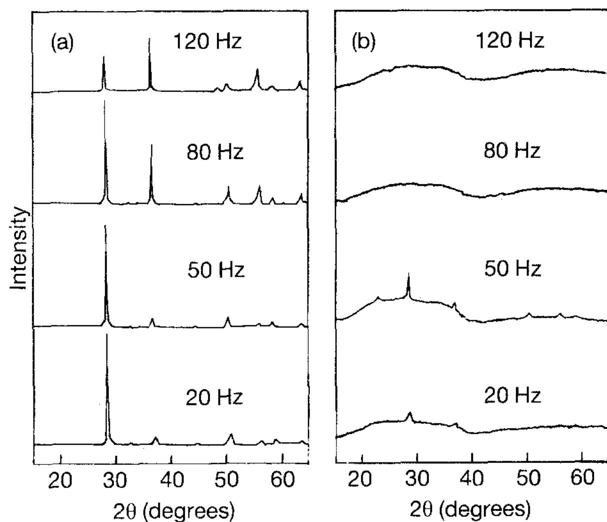

Figure 3 X-ray diffraction patterns of tantalum oxide films produced by laser CVD at laser fluences of 450 J m^{-2} (a) and 200 J m^{-2} (b). (Supply rate of $Ta(OCH_3)_5$, 200 mg h^{-1}; substrate temperature, 403 K.)

function of repetition rate, reactant supply rate and substrate temperature. At the same time, the deposition rate was also studied as a function of the same variables, so that some relationship might be indirectly found between the preferred orientation and the deposition rate and, consequently, between the preferred orientation and the supersaturation* at the surface of the substrate or growing deposit.

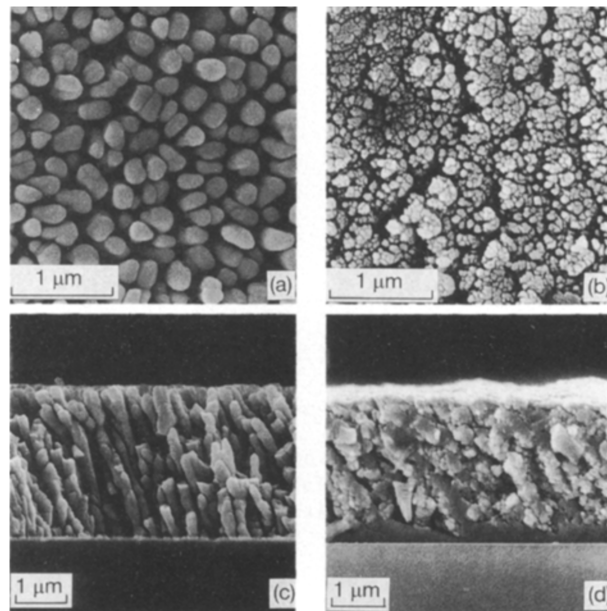

Figure 4 Scanning electron micrographs of the surface and the cross-section of tantalum oxide films produced by laser CVD at laser fluences of 450 J m^{-2} (a) and 200 J m^{-2} (b). (Repetition rate, 50 Hz; supply rate of $Ta(OCH_3)_5$, 200 mg h^{-1}; substrate temperature, 403 K.) Upper photographs, surface; lower photographs, cross-section.

The Lotgering's orientation factor (F_{hkl}) is defined by the equation:

$$F_{hkl} = (P_{hkl} - P^0_{hkl})/(1 - P^0_{hkl}),$$

where P_{hkl} is the ratio of the intensity of (h k l) reflection to the sum of all reflections in a scanned range of θ for an oriented deposit, and P^0_{hkl} is the corresponding value listed as standard in JCPDS Diffraction File 25-922. In a preliminary study, the factor was found to vary with deposit thickness, especially in the early stages of deposition; however, the variation was found to cease when the deposit became thicker than about 1 μm. Therefore, the orientation factor was calculated only for the deposits thicker than 1 μm.

Fig. 5 shows the relationship between orientation factor and repetition rate. The orientation factor was calculated from the data given in Fig. 3a. As can be seen from the figure, when the repetition rate was high, the (1 1 1 0) plane was preferentially oriented parallel to the substrate surface; in contrast to this, when the repetition rate was low, the (1 1 1 1) plane was oriented in the same way. The variation of the orientation with increasing repetition rate was also reflected in the surface appearance (Fig. 6).

Fig. 7 shows the effect of the repetition rate on the deposition rate as observed under different conditions of fluence. When the fluence was 450 J m^{-2}, an increase in the repetition rate resulted in a decrease in the deposition rate (solid circles in the figure). The

* The term supersaturation in this paper refers to such a high surface concentration of freshly-formed tantalum oxide in a state approximating to a gas or liquid that nucleation and growth of the oxide crystal are possible. The contribution of supersaturation to the rates of nucleation and crystal growth in other cases is discussed in References 19–22, for example.

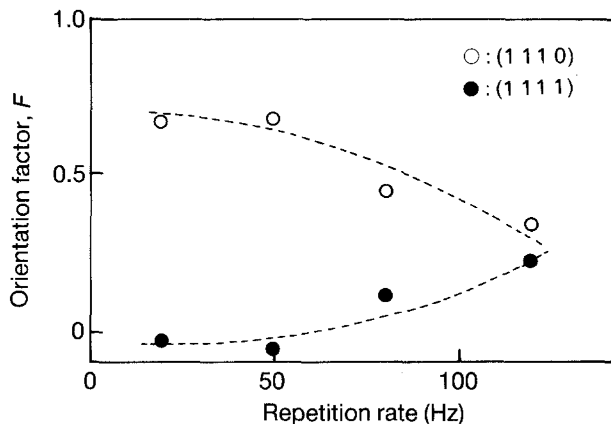

Figure 5 Relationship between orientation factor (F) and repetition rate in Hz. (Laser fluence, $450\ J\ m^{-2}$; substrate temperature, 403 K; supply rate of $Ta(OCH_3)_5$, $200\ mg\ h^{-1}$.)

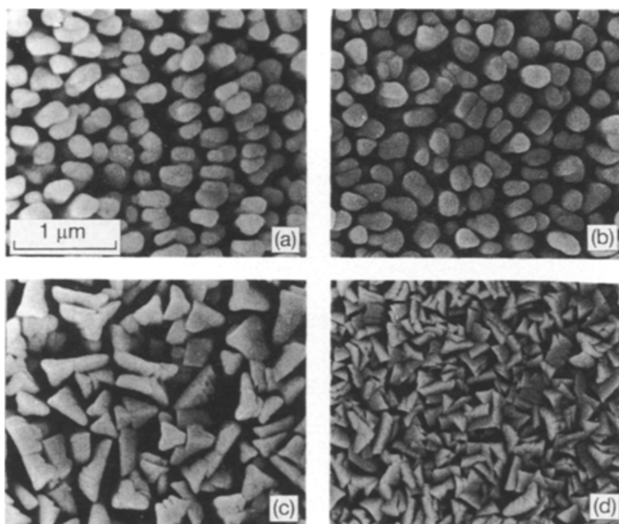

Figure 6 Scanning electron micrographs of the surface of tantalum oxide films produced at different repetition rates. (Laser fluence, $450\ J\ m^{-2}$; supply rate of $Ta(OCH_3)_5$, $200\ mg\ h^{-1}$; substrate temperature, 403 K.) Repetition rate in Hz: (a) 20, (b) 50, (c) 80 and (d) 120.

decrease of the deposition rate over the range of repetition rate above 70 Hz seems to be attributable to the depletion of the pentamethoxide vapour due to photolytic decomposition in the irradiated zone of the substrate surface and to the poor replenishment due to the slow diffusion of the reactant vapour into the zone. On the other hand, when the fluence was $200\ J\ m^{-2}$, the deposition rate was not affected by the repetition rate, possibly because the loss of reactant in the irradiated zone was balanced by the supply by diffusion of further reactant.

Fig. 8 shows the effect of the rate of supply of the pentamethoxide on the orientation factor under fixed conditions of fluence ($450\ J\ m^{-2}$), repetition rate (50 Hz) and substrate temperature (403 K). When the supply rate was small, the (1 1 1 1) plane was preferentially oriented parallel to the substrate surface; whereas the (1 1 1 0) plane was oriented in the same way when the supply rate was great. The corresponding variation of the deposition rate is shown in Fig. 9. As the supply rate was increased up to about $100\ mg\ h^{-1}$,

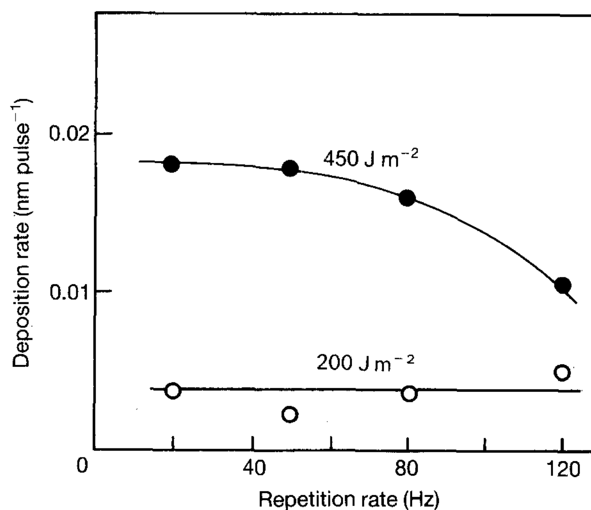

Figure 7 Dependence of deposition rate on repetition rate. (Substrate temperature, 403 K; supply rate of $Ta(OCH_3)_5$, $200\ mg\ h^{-1}$.)

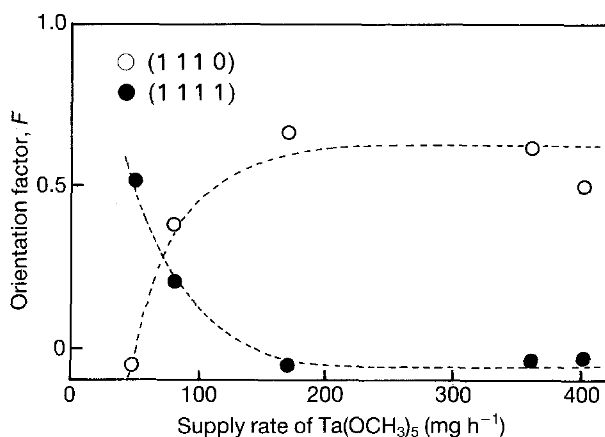

Figure 8 Relationship between orientation factor (F) and supply rate of $Ta(OCH_3)_5$. (Laser fluence, $450\ J\ m^{-2}$; repetition rate, 50 Hz; substrate temperature, 403 K.)

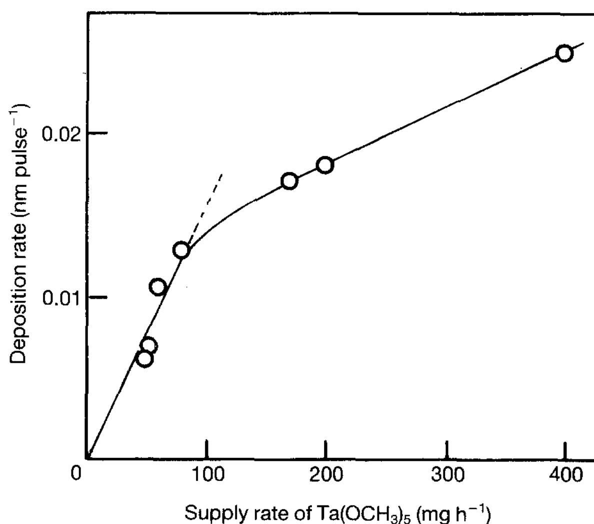

Figure 9 Dependence of deposition rate on supply rate of $Ta(OCH_3)_5$. (Laser fluence, $450\ J\ m^{-2}$; repetition rate, 50 Hz; substrate temperature, 403 K.)

the deposition rate increased rapidly with the supply rate; and as the supply rate was increased further, the deposition rate increased less rapidly. From a comparison of the two figures it follows that the preferred

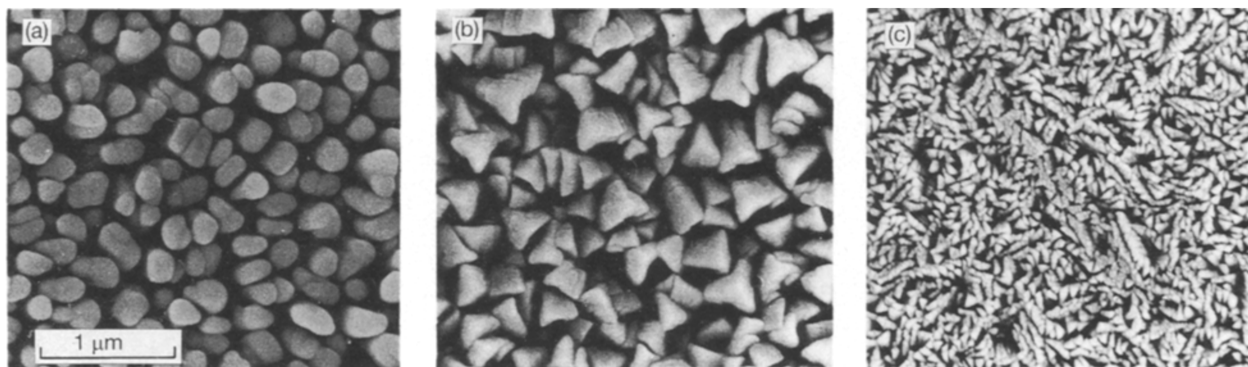

Figure 10 Scanning electron micrographs of the surface of tantalum oxide films produced at different supply rates of $Ta(OCH_3)_5$. (Laser fluence, 450 J m^{-2}; repetition rate, 50 Hz; substrate temperature, 403 K.) Supply rate of $Ta(OCH_3)_5$, mg h^{-1} (a) 200, (b) 60 and (c) 50.

orientation of the (1 1 1 1) plane was favoured when the deposition rate was low, whereas the preferred orientation of the (1 1 1 0) plane was favoured when the deposition rate was high.

The variation of the surface appearance of the deposit with the supply rate of the pentamethoxide is given in Fig. 10. It is similar to the variation shown in Fig. 6 as a function of the repetition rate, though the fibrous structure as shown in Fig. 10c could not be produced by changing the repetition rate, because of experimental limitation.

The effect of substrate temperature on the crystal orientation under fixed conditions of fluence (450 J m^{-2}), repetition rate (50 Hz) and the supply rate of the pentamethoxide (200 mg h^{-1}) is shown in Fig. 11. The (1 1 1 0) plane was preferentially oriented at low substrate temperatures, whereas the (1 1 1 1) plane was oriented preferentially at high substrate temperatures. The corresponding variation of the deposition rate is shown by open circles in Fig. 12. The deposition rate was almost independent of the substrate temperature below 620 K, but above this temperature it decreased drastically. In this case, the gas-phase thermal decomposition of the pentamethoxide was negligible, because the pentamethoxide supplied, when not irradiated, was scarcely decomposed over the temperature range studied, as is shown by open square marks in Fig. 12. From a comparison of the two figures, it follows that the preferred orientation of the (1 1 1 0) plane was favoured at high deposition rates, whereas the preferred orientation of the (1 1 1 1) plane was favoured at low deposition rates. In this connection it must be added that the same drastic change in deposition rate at temperatures above 620 K, as shown in Fig. 12, has not been observed in the photo-CVD reaction effected by radiation from a low-pressure mercury lamp [15], i.e. by radiation less powerful than the radiation used in this work.

Variation of the surface appearance of the deposit with substrate temperature is given in Fig. 13. It is similar to those observed by varying the repetition rate (Fig. 6) as well as by varying the supply rate of the pentamethoxide (Fig. 10).

From the above results it can be seen that, whichever factor among the three—repetition rate, supply rate of the pentamethoxide and substrate temperature—may be varied, the preferred orientation of the (1 1 1 0) plane is favoured when the deposition rate is great. Since the relationship, given in Fig. 9, between the deposition rate and the supply rate of the pentamethoxide corresponds roughly to the relationship between the deposition rate and supersaturation, it

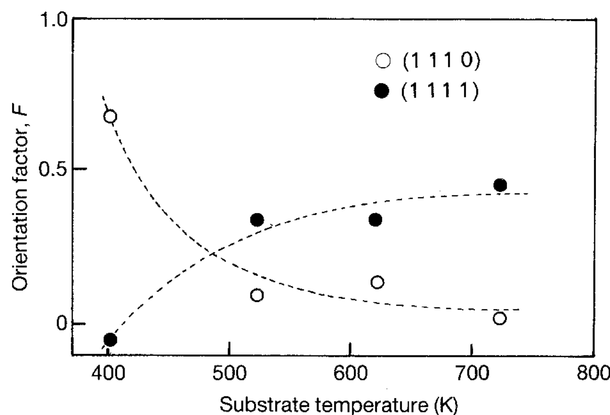

Figure 11 Relationship between orientation factor (F) and substrate temperature. (Laser fluence, 450 J m^{-2}; repetition rate, 50 Hz; supply rate of $Ta(OCH_3)_5$, 200 mg h^{-1}.)

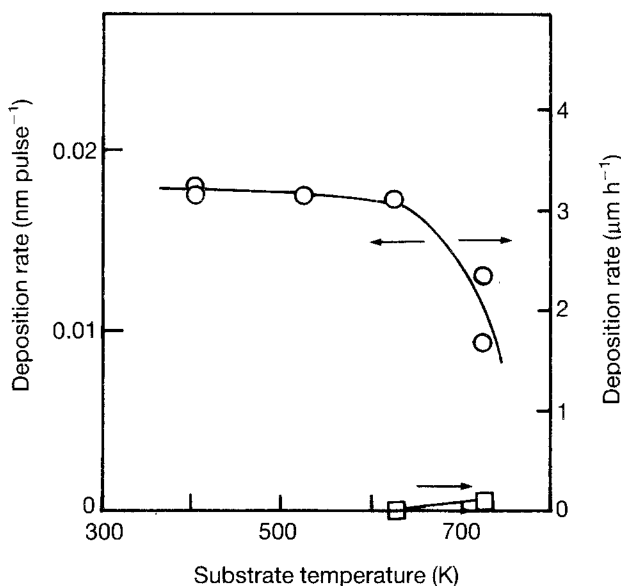

Figure 12 Dependence of deposition rate on substrate temperature. (Laser fluence, 450 J m^{-2}; repetition rate, 50 Hz; supply rate of $Ta(OCH_3)_5$, 200 mg h^{-1}.) The open squares represent the rate of deposition due to thermal decomposition without laser irradiation.

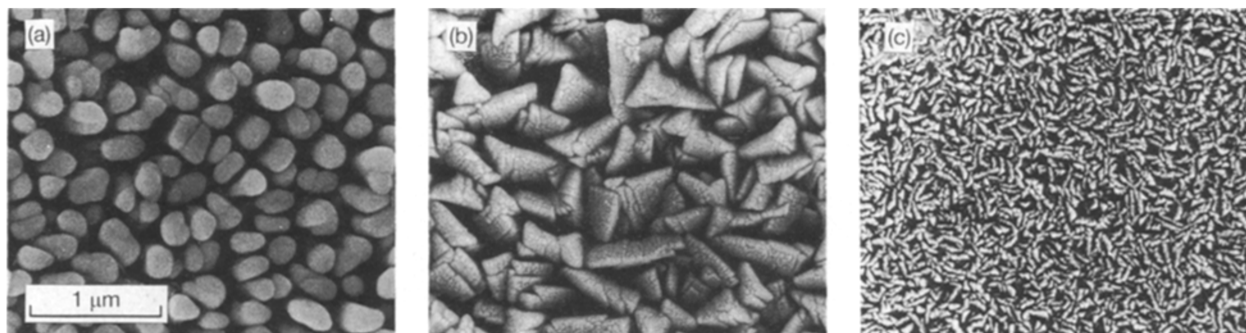

Figure 13 Scanning electron micrographs of the surface of deposited films obtained at different substrate temperatures. (Laser fluence, 450 J m^{-2}; repetition rate, 50 Hz; supply rate of $Ta(OCH_3)_5$, 200 mg h^{-1}.) Substrate temperature, K: (a) 423, (b) 623 and (c) 723.

may be qualitatively stated that the supersaturation at the surface of the substrate or growing deposit has a significant effect on the crystalline forms and preferred orientation of tantalum oxide deposits. Apparently, however, the elucidation of the mechanism of crystallization and crystal growth in photo-CVD must await further research.

4. Conclusion

Tantalum oxide films have been produced on a substrate by the photolytic decomposition of tantalum pentamethoxide with the use of a KrF laser beam. Deposits of highly-oriented crystals, exhibiting an XRD pattern corresponding to that of β-Ta_2O_5, were produced at a high laser fluence, whereas deposits exhibiting a weak XRD pattern were produced at a low fluence. The preferred orientation of the former deposits was governed by the laser repetition rate, the supply rate of the pentamethoxide and the substrate temperature. Possibly, the preferred orientation may be explained in terms of the supersaturation.

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