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Recovery of stoichiometry of Ta_2O_5 prepared by KrF excimer laser CVD from tantalum methoxide using microwave discharge of oxygen gas

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A flow of oxygen gas activated by passing through a microwave discharge plasma in a 100 and 200 W field was introduced into a deposition chamber for tantalum oxide deposition by KrF laser photolysis of $Ta(OCH_3)_5$, and the change of the non-stoichiometry of deposit was examined under the laser condition of 120 Hz and 200 $J m^{-2}$. The stoichiometry of the deposit could be improved to a value of about 90% under the condition of rather low supply rate of $Ta(OCH_3)_5$ (100 mg h^{-1}). An effect of post-treatment laser following chemical vapour deposition (CVD) by KrF laser and/or microwave discharge of oxygen gas was also investigated, and it was found that activated oxygen species formed by KrF laser irradiation in an oxygen gas atmosphere which passed through a microwave discharge was effective in enhancing the oxidation of non-stoichiometric tantalum oxide prepared by KrF laser CVD.

1. Introduction

Tantalum oxide is receiving considerable attention as a storage capacitor in very large scale circuit (VLSI) [1, 2], optical devices [3, 4] piezoelectric films [5] and as a protective coating material for chemical equipment against a highly corrosive environment [6]. The authors have already reported that tantalum oxide film grows phototropically by KrF excimer laser chemical vapour deposition (CVD) (LCVD) from tantalum pentamethoxide [$Ta(OCH_3)_5$] [7] and examined an effect of deposition conditions on the structure, morphology and non-stoichiometry of deposits [8–10]. Tight and dense structures were obtained at lower laser fluence and higher laser repetition rate [9]. Though the X-ray diffraction (XRD) patterns of films obtained corresponded to β-Ta_2O_5, it was found that the oxygen content of the deposits is less than the stoichiometric value (Ta_2O_5). The oxygen defects in the films might increase leak-current of the film, which is a serious problem in the above applications.

The non-stoichiometry of the films increased with the laser fluence, to reach a maximum value of about 20% in the laser fluence range 150–250 $J m^{-2}$ and then decreased [10]. From the view point of non-stoichiometry, it seems to be favourable to use either relatively low (lower than 100 $J m^{-2}$) laser fluences or high (higher than 300 $J m^{-2}$) fluences so as to obtain the near-stoichiometric tantalum oxide films. However, higher fluence brought about columnar crystal growth and was not suitable for obtaining tight and dense films [9]. Tight and dense films could be obtained at lower fluence, but the rate of deposition at the low fluence was quite small. It is required that stoichiometric and dense tantalum oxide be obtained at a reasonable deposition rate.

The objectives of the present paper are to improve the stoichiometry of tantalum oxide films by KrF laser CVD (LCVD) from $Ta(OCH_3)_5$ by enhancing the oxidation of tantalum in the film during or after the deposition process.

2. Experimental procedure

Details of the experimental setup for LCVD was described in a previous paper [8], but the path of the source gases has been improved as shown in Fig. 1. A coaxial nozzle, consisting of a 6 mm nozzle set with a larger 12 mm nozzle, was placed just above the substrate (distance of the tip from the substrate was 3 mm) to concentrate source gases onto the substrate. Tantalum pentamethoxide [$Ta(OCH_3)_5$] was used as a source material. It was sublimated in an oil bath and carried into the deposition chamber (30 cm in diameter; 30 cm in height) with a He carrier gas at a flow rate of 50 standard $cm^3 min^{-1}$ through the inner nozzle. The supply rate of $Ta(OCH_3)_5$ into the chamber, S_R, was monitored by load–cell weighing. It was adjusted to 100–400 mg h^{-1} by changing the temperature of the oil bath, T_{sub}, between the range 383–403 K.

Oxygen was introduced through the outer nozzle at a flow rate of 50 standard $cm^3 min^{-1}$ to enhance the

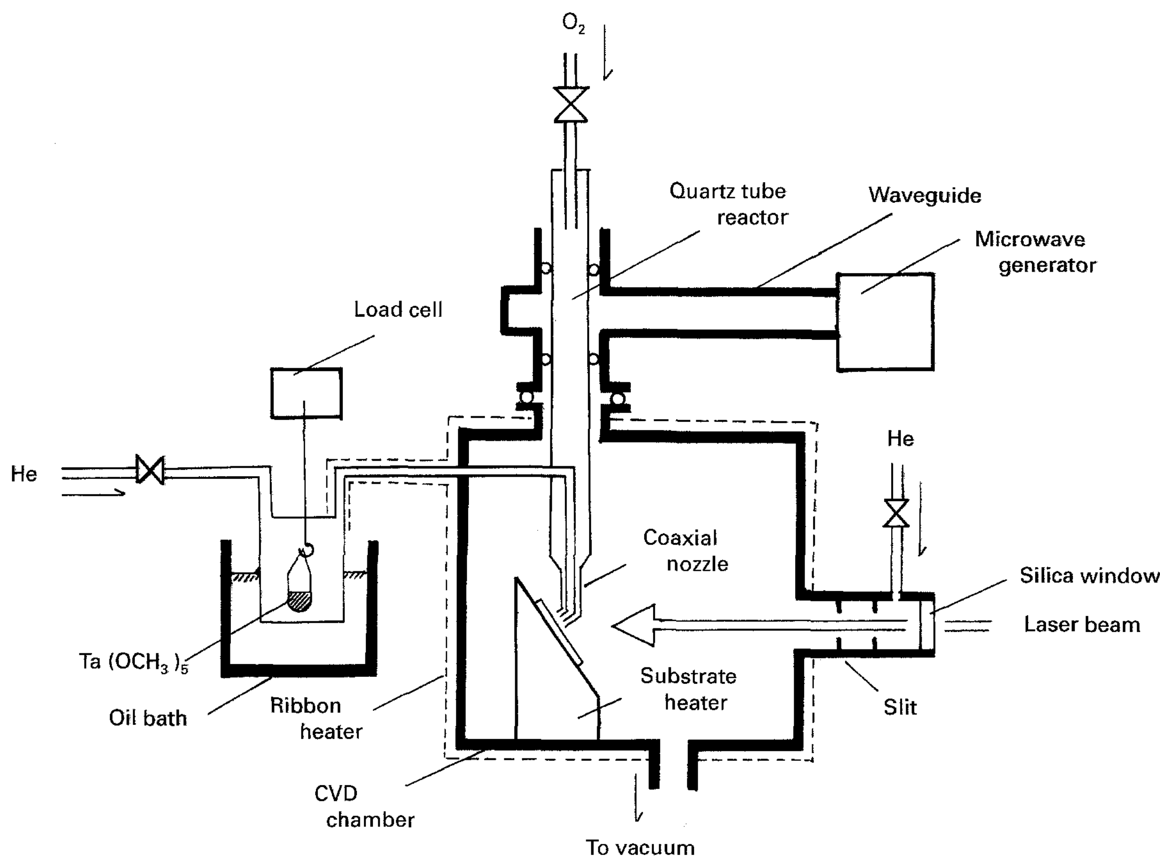


Figure 1 Schematic representation of the used source gas path for laser CVD experiments.

oxidation of the tantalum in the film during or after the deposition process. In some experiments, the flow of oxygen gas was forced to pass through a microwave discharge before passing through the coaxial nozzle so as to generate activated oxygen species. The microwave discharge was produced using a flow-tube reactor, made of a 25 mm i.d. quartz tube passing through a 2.45 GHz microwave cavity. The power dissipated in the plasma, P_P, calculated from the difference in incident and reflected power was in the range 100–200 W. This distance between the discharge zone and the substrate in the present work was about 35 cm.

During the deposition process, He purge gas was also introduced just behind the laser entrance window of the deposition chamber at a flow rate of 50 standard $cm^3 min^{-1}$ to prevent the source gas from approaching the window. The total pressure of the deposition chamber was maintained at 133 Pa.

A commercially pure iron substrate, placed in the deposition chamber, was heated to 403 K. It was irradiated by the unfocused KrF laser (Lumonics HE-460-SM-A) through a window at a repetition rate, R_R of 120 Hz. The laser fluence, F_L, on the substrate, monitored by a laser power meter (Scientech 38-2UV5), was adjusted to 200 $J m^{-2}$, where tight and dense deposits could be obtained at a relatively high rate, unless otherwise stated. The incident angle of laser beam to the substrate was 60°.

The elemental analysis of the films obtained was carried out by *X*-ray photoelectron spectra (XPS) measurements using a Shimadzu ESCA-850 electronic spectrometer. The chemical shift of Ta 4*f* XPS spectra of deposited oxide films compared to stoichiometric Ta_2O_5 was ascribed to the oxygen deficiency of films because the carbon content of films was less than the background contamination level of the analysis (a few per cent). The ratio of the content of oxygen to tantalum in films could be determined by peak deconvolution of the XPS curves by procedures stated previously [10], assuming that the chemical shift of Ta 4*f* increases monotonously with the valence of the Ta atom. The conventional method using the intensities of the peaks of oxygen and tantalum was not used here because there might be experimental errors due to the contribution of XPS from the uncoated area of the substrate and surface oxidation and/or contamination after deposition before analysis. MgK_α ($h\nu = 1253$ eV) radiation was used for excitation of the photoelectrons. The depth profiles of the samples were determined by Ar ion etching at an acceleration potential of 2 kV with a current of 4 μA under an argon pressure of 4×10^{-4} Pa.

3. Results and discussion

3.1. Effect of activated oxygen species during CVD

The films produced under various conditions were semitransparent and ranged in colour from brown to (blue-) black. Open circles in Fig. 2 show the effect of laser fluence on the deposition rate in the case of He carrier gas under the conditions of $R_R = 120$ Hz, $S_R = 400$ $mg h^{-1}$ and a substrate temperature, T_{sub}, of 403 K. Also shown in the figure by closed circles, are the results where oxygen gas, on which microwave discharge was implemented, was introduced into the

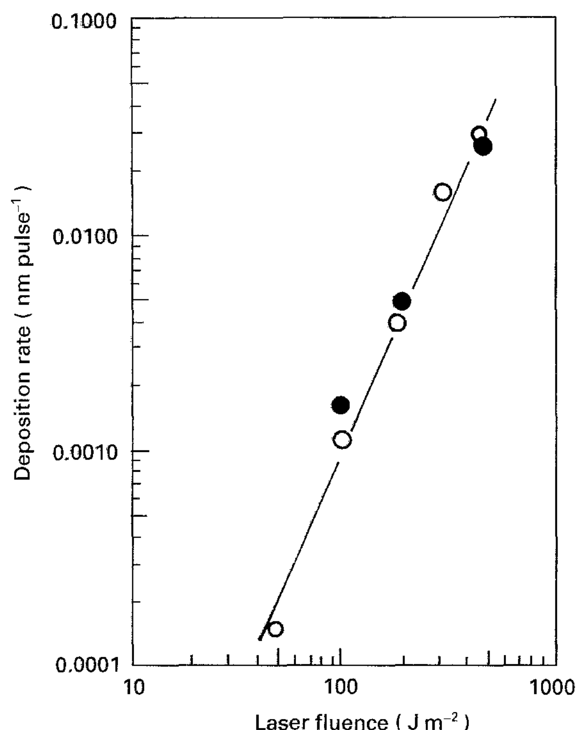


Figure 2 Dependence of deposition rate on laser fluence (repetition rate, 120 Hz; substrate temperature, 403 K; supply rate of $Ta(OCH_3)_5$, 400 mg h^{-1}) : rates of deposition in the case of (○) helium carrier gas and (●) O_2, passing through a microwave discharge of 100 W introduced into the chamber.

chamber. The deposition rate increased approximately in proportion to the third power of the fluence, as already described [8], though the use of a nozzle to concentrate the source gas onto the substrate increased the deposition rate remarkably compared to previous work [8]. The deposition rate was not drastically changed by the implementation of plasma on the oxygen gas as seen from the comparison of open and closed circles in Fig. 2.

Fig. 3 presents the effect of the implementation of microwave plasma on oxygen gas during the LCVD process on the XPS of the deposited films. It shows the Ta 4*f* XPS of films after Ar ion etching for 40 min. The relative intensity at the low binding energy region, corresponding to lower oxidation state, becomes smaller when microwave plasma was implemented in the case where the supply rate of $Ta(OCH_3)_5$ was low ($S_R = 100$ mg h^{-1}, see Fig. 3a), while little effect was observed for the case that was higher ($S_R = 400$ mg h^{-1}, Fig. 3b). The non-stoichiometry of the films, which was determined by peak-deconvolution of the curves in Fig. 3, taking the selective removal of the lighter element in the compound of the films, i.e. oxygen, by Ar ion etching into account, is shown in Fig. 4 as a function of the microwave power implemented on the oxygen gas. Here, the stoichiometry index, $1-x$, is defined so as to express the chemical composition of the films in the chemical formula of $Ta_2O_{5(1-x)}$. The films obtained at a laser fluence of 200 J m^{-2} are about 20% deficient in oxygen compared to stoichiometric Ta_2O_5, independently of the supply rate, or the partial pressure, of $Ta(OCH_3)_5$ in the range of the present experiment (see the closed square and the closed circle in Fig. 4).

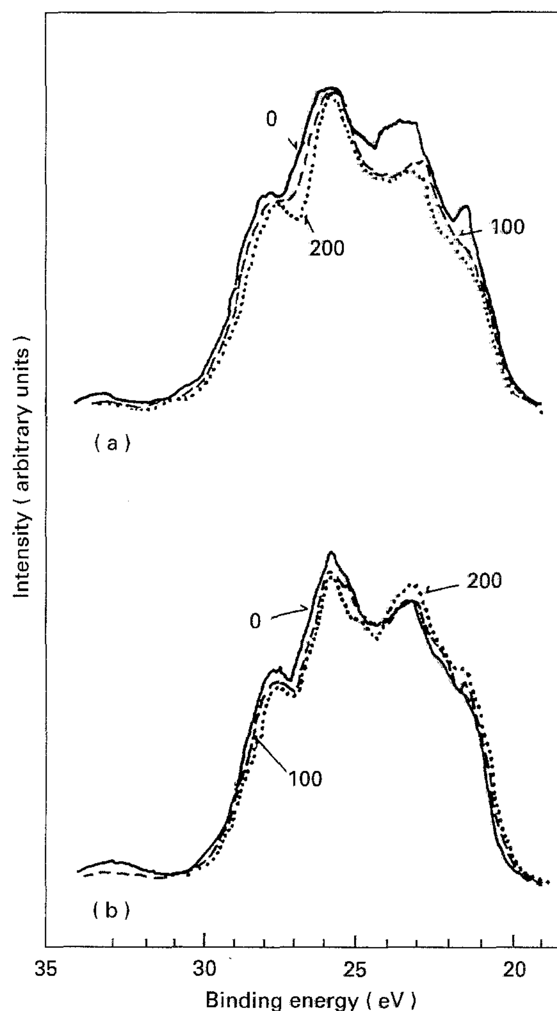


Figure 3 Effect of microwave plasma implementation on the oxygen gas on the XPS of films deposited. The numeric values in the figure indicate the microwave plasma power in W. Deposits were obtained under the following conditions: laser fluence, 200 J m^{-2}; repetition rate, 120 Hz; substrate temperature, 403 K; supply rate of $Ta(OCH_3)_5$ in mg h^{-1}, (a) 100 and (b) 400.

The mixing of oxygen gas in the CVD atmosphere had no effect on the composition of films, either. (Compare, for example, the closed circle and the open circle at the microwave power of 0 W.) However, the stoichiometry of the films could be recovered by the activated oxygen gas produced by microwave plasma at the rather low supply rate of $Ta(OCH_3)_5$ ($S_R = 100$ mg h^{-1}) to about 90% (see open circles). In the case of a higher supply rate of $Ta(OCH_3)_5$ ($S_R = 400$ mg h^{-1}), the effect could not be detected and it seemed that the ratio of the concentration of activated oxygen in the CVD atmosphere to that of the precursor, $Ta(OCH_3)_5$, should be large.

3.2. Effect of film oxidation in an atmosphere containing activated oxygen species after CVD

Since, as noted above, relatively dense tantalum oxide film obtained at a reasonable deposition rate (about 0.005 nm pulse^{-1} = 2.16 μm h^{-1}) under a relatively high repetition rate ($R_R = 120$ Hz) and low fluence ($F_L = 200$ J m^{-2}) was oxygen deficient even if the microwave power was implemented on oxygen in an

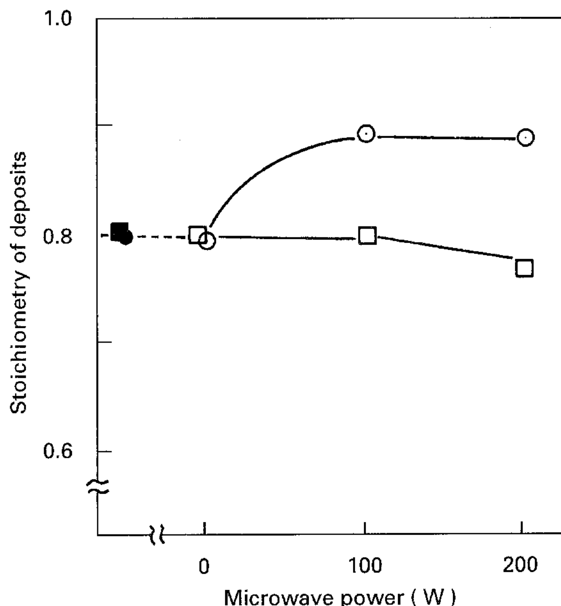


Figure 4 Dependence of stoichiometry of the films on microwave plasma power. The ordinates indicate the values of "1–x" in the chemical formulae of deposits expressed in the form of $Ta_2O_{5(1-x)}$. Films were obtained under the following conditions: laser fluence, 200 J m^{-2}; repetition rate, 120 Hz; substrate temperature, 403 K; Supply rate of $Ta(OCH_3)_5$, 100 mg h^{-1} (○) or 400 mg h^{-1} (□). Closed symbols indicate, values for the films obtained by LCVD without oxygen gas.

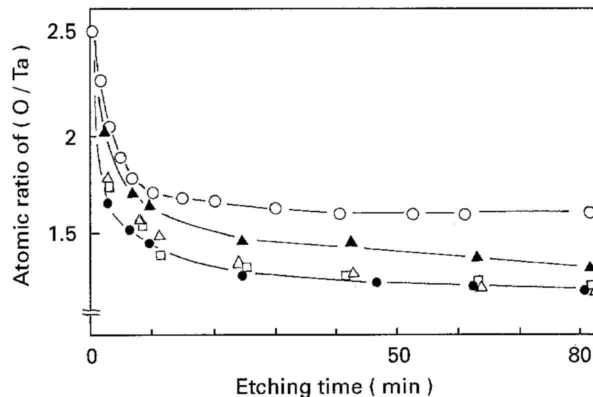


Figure 5 Change of the atomic ratio (O/Ta) of analysed surface with Ar etching determined by the chemical shift of $Ta(4f_{7/2,5/2})$: (○) stoichiometric Ta_2O_5 obtained by rf sputtering deposition; (●) as-deposited film [obtained under laser fluence, 200 J m^{-2}; repetition rate, 120 Hz; supply rate of $Ta(OCH_3)_5$, 400 mg h^{-1}; carrier gas, 100 cm^3 min^{-1} of He; substrate temperature, 403 K] ; (□) films obtained under the above conditions followed by exposure to KrF laser irradiation of 450 J m^{-2}, 50 Hz for 30 min at room temperature; (△) films obtained under the above conditions followed by exposure to an atmosphere of activated oxygen produced by microwave discharge of 2.45 GHz, 100 W for 30 min; and (▲) films obtained under the above conditions followed by KrF laser irradiation of 450 J m^{-2}, 50 Hz, in an atmosphere of activated oxygen produced by microwave discharge of 2.45 GHz, 100 W for 30 min.

ambient gas especially in the case of a high supply rate of $Ta(OCH_3)_5$, oxidation after deposition was also tried. It is well known that tantalum can be oxidized fully by high temperature oxidation at about 700 K or above, but resulting in pulverization. Therefore, high temperature oxidation is not a suitable method for these purposes and oxidation at lower temperature was tried in an atmosphere containing activated oxygen species.

The activated oxygen was produced by a similar method with the *in situ* oxidation during CVD, stated above. Oxygen was forced to pass through a microwave discharge and then introduced through the outer nozzle of the coaxial nozzle at a flow rate of 50 standard cm^3 min^{-1}. Helium gas was introduced into the chamber behind the laser entrance window at a flow rate of 50 standard cm^3 min^{-1}. The total pressure in the deposition chamber was maintained at 133 Pa. In some experiments, the samples were irradiated by a KrF laser through the window at a repetition rate of 120 Hz.

Fig. 5 shows the change of the atomic ratio of oxygen to tantalum, A_R, on the analysed surface of films with the etching process, determined by peak deconvolution of the XPS curves as stated before, where the films were prepared at $F_L = 200$ J m^{-1}, $R_R = 120$ Hz, $S_R = 400$ mg h^{-1} and $T_{sub} = 403$ K. The estimated etching rate was of the order of 2 nm min^{-1}. A_R of each film decreases with etching time because of selective removal of the lighter element (oxygen) in the films by high energy argon ions compared to the heavier element (tantalum). However, the decreasing rate of A_R seems to be dependent on the preparation methods of the films, as seen from the figure.

A_R of stoichiometric Ta_2O_5, shown by the open circles in the figure, decreases from an initial value of 2.5 (Ta_2O_5) to about 1.6 with the argon-ion etching process, where the sample was obtained by radio frequency (rf) magnetron sputtering deposition using a pressed Ta_2O_5 powder target in an atmosphere of argon and oxygen (volume ratio = 67:33, total pressure = 1.1 Pa) with a power of 150 W. On the contrary, A_R of the LCVDed tantalum oxide deposit, shown by the closed circles, decreases more rapidly from 2.5 to 1.25 with the etching process. This is nearly the same for the samples which were exposed after the LCVD process in

1. The KrF laser irradiation of 450 J m^{-2} in the atmosphere containing oxygen gas, or
2. The oxidation atmosphere by oxygen gas flow passing through a microwave discharge of 100 W,

shown by open squares and open triangles, respectively. However, the behaviour is different for the sample which was irradiated by the KrF laser of 450 J m^{-2} in the atmosphere of oxygen gas after passing through a microwave discharge of 100 W, shown by closed triangles.

Clearly, the decrease in A_R value for that sample is slow compared to the non-treated LCVDed sample, and the Ta in that sample is in a more oxidized state, which indicates the recovery of the stoichiometry of the film was attained in a region more than 0.15 μm deep. The morphology of the film was not appreciably varied by this treatment, as shown by comparison of Fig. 6a and b, which presents the cross-sectional scanning electron microscope (SEM) images of the LCVDed film before and after treatment.

The changes of electric conductivity of the LCVDed film by this treatment are presented in Fig. 7. It is obvious from the figure that this treatment increases the electric resistance by one order of magnitude,

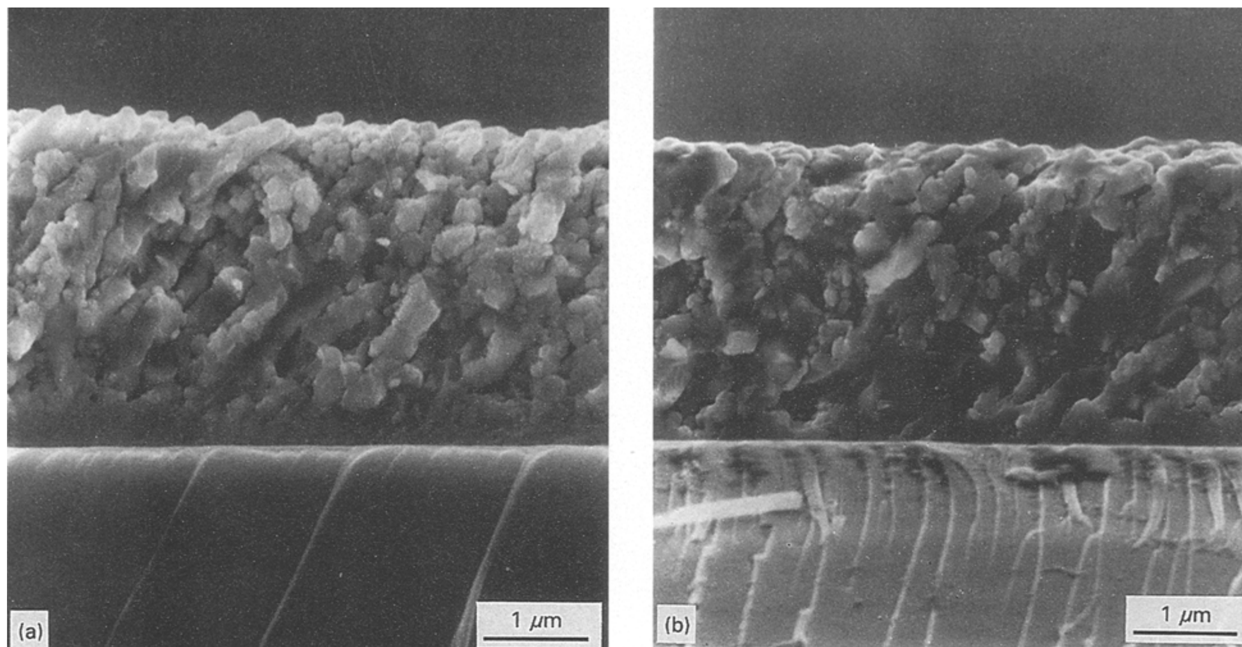


Figure 6 Scanning electron micrographs of the cross-section of tantalum oxide films produced by laser CVD (a) before and (b) after exposure to KrF laser irradiation of 450 $J m^{-2}$, 50 Hz, in an atmosphere of activated oxygen produced by microwave discharge of 2.45 GHz, 100 W for 30 min. Deposition conditions: laser fluence, 200 $J m^{-2}$; repetition rate, 120 Hz; substrate temperature, 403 K; supply rate of $Ta(OCH_3)_5$, 400 $mg h^{-1}$.

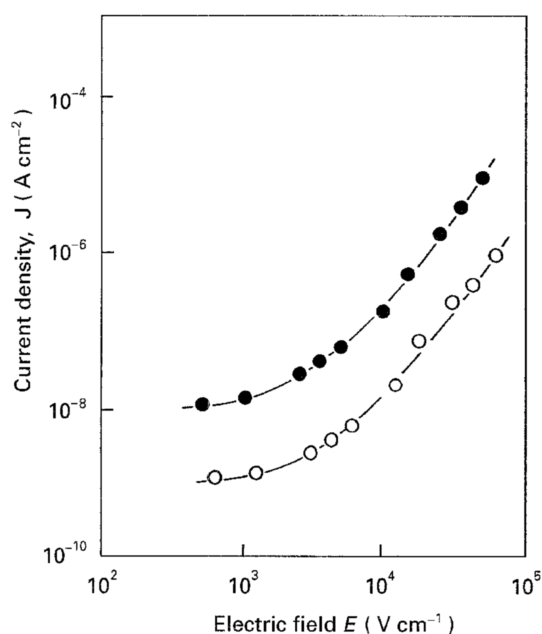
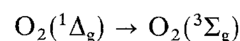


Figure 7 Relation between current density and applied electric field of as-deposited tantalum oxide film and post-treated film under the conditions as in Fig. 6: (●) as-deposited film and (○) post-treated film.

though it is still smaller than the value expected from stoichiometric Ta_2O_5 [11–13], which was thought to be brought about by compensation of the oxygen defects.

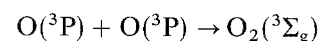
3.3. Discussion on the oxygen species in microwave treatment

The stoichiometry of the deposited oxide film could be improved both by *in situ* oxidation during LCVD and by post-treatment with KrF laser irradiation in an atmosphere containing activated species of oxygen produced by microwave plasma. A number of studies have been carried out on the activated oxygen species produced by electric discharge of oxygen gas and the following species have been considered; oxygen ion ($O_2^+, O^+, O^-, O_2^-, \ldots,$), oxygen molecule [$^3\Sigma_g$ (ground state), $^1\Delta_g$, $^1\Sigma_g$], and oxygen atom [^3P (ground state), ^1D, ^1S] [14, 15]. Most of them are, however, easily deactivated by homogeneous recombination with ambient gas of relatively high pressure, as in the present study, and/or by surface recombination on silica or metallic materials. The activated products of a microwave discharge in an O_2 stream detected by electron paramagnetic resonance spectroscopy are $O_2(^1\Delta_g)$ and $O(^3P)$ and the conversion efficiency of oxygen gas in similar conditions (86 Pa of oxygen, 100 W of microwave power) was estimated to be 7% for $O_2(^1\Delta_g)$ and 3% for $O(^3P)$ [16]. These are thought to react with each other to make $O_2(^3\Sigma_g)$ and O_3 by the following reactions

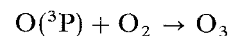


$$O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g)$$

$$O_2(^1\Delta_g) \rightarrow O(^3P) + O(^3P)$$



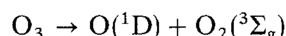
$$O(^3P) + O(^3P) \rightarrow O_2(^3\Sigma_g)$$



$$O(^3P) + O_2 \rightarrow O_3$$

O_3 was detected, though not quantitatively, downstream of the present experimental apparatus during the CVD experiment, with a microwave discharge, because iodine was isolated from KI solution by an exhausted gas from the vacuum system. O_3, however, seems to have little effect on the oxidation of tantalum oxide because no remarkable effect on surface composition was observed, as is shown by open triangles in Fig. 5. Increase in oxygen in the deposit was observed as shown in Fig. 4, only when the KrF laser was irradiated in that atmosphere.

It is admitted that $O(^1D)$ can be formed by the irradiation of ultraviolet (u.v.) light on O_3 gas by the following reaction



$$O_3 \rightarrow O(^1D) + O_2(^3\Sigma_g)$$

The threshold wavelength for the formation of atomic oxygen (^1D) from O_3 is 411 nm [17] and thermal decomposition of O_3 can produce oxygen atoms only in the state of $O(^3P)$ without u.v. irradiation. Therefore, it is speculated that the existence of $O(^1D)$ plays an important role for improvement of the stoichiometry of CVDed tantalum oxide film, as is suggested in the intensive study by Tanimoto *et al.* [18] on the leakage current reduction of tantalum oxide on silicon substrate by low pressure mercury lamp.

4. Conclusions

In order to improve the stoichiometry of tantalum oxide film by KrF laser photolysis of $Ta(OCH_3)_5$, an effect of the activated oxygen was examined during and after deposition. A flow of oxygen gas which passed through a microwave discharge of 100 or 200 W was introduced into the deposition chamber under the laser condition of 120 Hz and 200 $J\,m^{-2}$, which was a favourable condition to obtain a dense deposit. The stoichiometry of the deposit was improved to a value of about 90% under the condition of rather low supply rate of $Ta(OCH_3)_5$ (100 $mg\,h^{-1}$). From the investigation of the effect of post-treatment of deposits by KrF laser and/or microwave discharge of oxygen gas, it was found that activated oxygen species formed by KrF laser irradiation in an atmosphere of oxygen gas which passed through a microwave discharge was effective in enhancing the oxidation of non-stoichiometric tantalum oxide prepared by KrF laser CVD. Electric resistance of the LCVDed film was increased by one order of magnitude with this treatment.

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