(BL8A)

Homoepitaxial growth of ZnTe by synchrotron radiation using metalorganic sources

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Photo-excited growth using synchrotron radiation is promising as a new non-thermal technique. Actually, we have already demonstrated that the deposition of ZnTe using diethylzinc (DEZn) and diethyltelluride (DETe) occurs epitaxially on the (100) oriented GaAs substrate even at room temperature. However, it was very difficult to observe the photoluminescence from the ZnTe film grown on GaAs substrate, which suggests that the film exhibits inferior optical property. In this study, we have investigated homoepitaxial growth of ZnTe in order to improve optical property of the layer. We dealt with the effect of the transport rate of source materials upon the ZnTe growth using DEZn and DETe, since the partial pressure ratio of the alkyls is an important factor that not only gives valuable information on the associated growth process but also influences optical property of the layer. The experiments were carried out using the SR beam line, BL8A. The (100) orientated ZnTe wafers synthesized in our laboratory by Bridgman method were employed as substrates. The incident SR beam irradiates the sample surface perpendicularly. The deposition was carried out at a very low pressure of $\sim 10^{-5}$ Torr in the growth chamber. In Fig. 1, the relationship is shown between the growth rate and DETe transport rate. Here, the results obtained for DEZn transport rates of 0.1 μmol/min and 0.05 μmol/min are plotted in the same figure in order to investigate the effect of DEZn transport rate upon the growth rate. The growth rate increases sublinearly with increasing DETe transport rate and it becomes saturated, as shown for a DEZn transport rate of 0.1 μmol/min. The almost linear relationship between the growth rate and DETe transport rate means that rate limiting step is due to the supply of DETe. On the other hand, the saturated tendency of the growth rate indicates that the growth rate is limited by the supply of DEZn, in good agreement with the fact that the growth rate decreases with decreasing DEZn transport rate in this region. From the relationship between the growth rate and DEZn transport rate when DETe transport rate was kept at 1 μ mol/min, we have already shown that the growth rate increases rapidly with increaing DEZn transport rate and then it eventually becomes saturated beyond a very low transport rate of 0.1 μ mol/min (see fig.2). Thus, a significant difference can be found in the growth rate behavior between the results shown in figs.1 and 2. The growth rate of ZnTe will directly depend upon the adsorption coefficient of precursors, since the growth rate is decreased with increasing the substrate temperature due to the decrease of adsorption coefficient as shown in fig.3. The difference in the growth rate behavior under two conditions shown in fig.1 and fig.2 suggests that adsorption coefficient of DEZn is very high compared to DETe. We have measured the photoluminescence spectra at 4.2 K under 458nm Ar^+ laser excitation in order to assess the optical properties of ZnTe films. The penetration depth of the laser light is about one third of a μm. Therefore, ZnTe films with thickness between 1.5 and 2 μm were investigated in order to avoid influence from substrate. Figure 4 shows typical photoluminescence spectra of the ZnTe films. The excitonic emission (I_a) at 2.375 eV and the strong deep level emissions with two broad bands centered at around 2.1 eV and 1.85 eV were detected as the

main feature of the spectrum (fig. 4(a)). The I_a line is attributed to shallow accepors, namely Li, Cu, Na. This peak is observed widely for undoped ZnTe grown by another growth methods. The deep-level luminescence obtained here can be found in the experimental results by Tews et al., who have attempted laser-induced diffusion in ZnTe with Cl. SR illumination looks to be effective in enhancing the decomposition of the impurity molecules such as Cl related compound. However, it is not at least difficult to suppress defects associated with the deep-level emissions by choosing a suitable growth condition. As shown in fig. 4(b), the deep-level emissions almost vanishes in the photoluminescence spectrum of epitaxial film deposited at a reduced growth rate (about 0.06 Å/mA·min). The spectrum was composed of strong I_a line and relatively weak donor-acceptor pair band. Although we have not yet attempted to optimize the various growth parameters to obtain the ZnTe film of high quality, it should be noted that near band gap luminescence can be observed even in the ZnTe epitaxial films grown at room temperature.

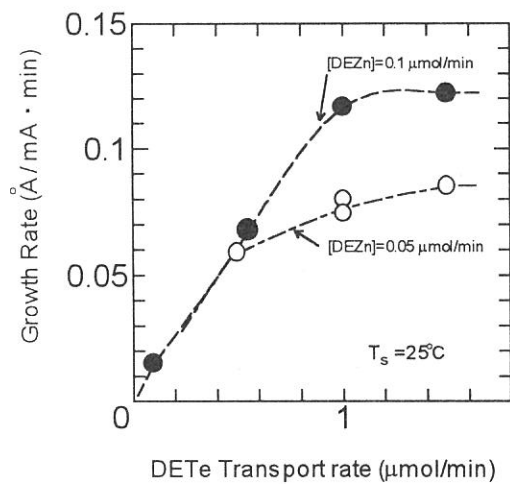

Fig. 1. Growth rate of ZnTe film versus DEZn transport rate.

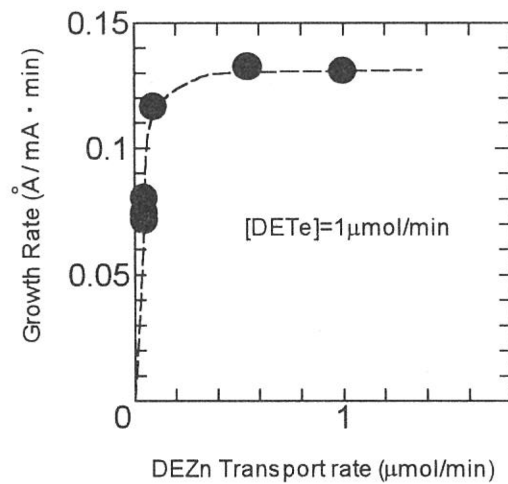

Fig.2. Growth rate of ZnTe film versus DETe transport rate.

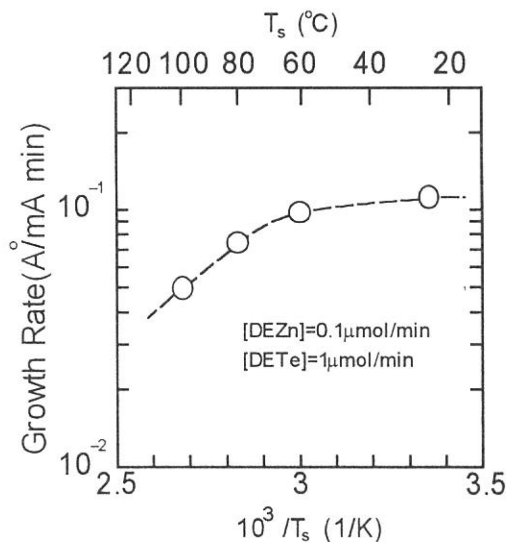

Fig.3. Growth rate of ZnTe versus substrate temperature.

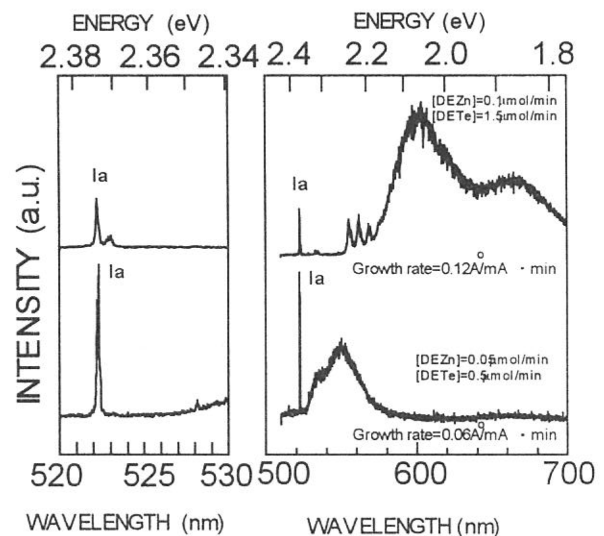

Fig. 4. Typical photoluminescence spectra of ZnTe films.

(BL8A)

Synchrotron radiation etching of diamonds

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Diamonds can be etched with the aid of synchrotron radiation(SR) excitation in the atmosphere of oxygen gas[1-2]. This is expected to become one of the potential techniques for micro-fabrication of diamonds.

The experiment was performed at the beamline BL8A of UVSOR which a reaction chamber with a differential pumping system was attached to. Etchant gas was filled in the chamber. NO_2 and H_2O were used as etchant besides O_2, because NO_2 is considered to be more reactive than O_2 for oxidization. The pressure of the gas in the reaction chamber was 0.1 torr and the diamond sample was kept in the room temperature. The etch rates for the three different etchants are listed in table 1. We see that the rate for H_2O is almost a half of that for O_2. Furthermore, no clear difference of the etch rate can be seen between O_2 and NO_2. This seems to show that atomic oxygen dissociated from the molecules may contribute to etching, but not the molecules themselves.

We can expect from the above result that a high concentration of atomic oxygen may result in a high etch rate of diamond. A radical generator by means of microwave discharge was attached to the reaction chamber in the direction perpendicular to SR. A nickel mesh mask was placed in the front of the sample. Oxygen gas was introduced into the radical generator operated in the power of 300 W. The surface of diamond taken by AFM is shown in Fig.2. The dose of SR was 10,000 mA·min and the pressure in the chamber was 1×10^{-4} torr. The temperature of the surface rose up to 80℃ because of irradiation of SR and heat from the radical generator, although the diamond sample was cooled by liquid nitrogen. We can see from the AFM micrograph that the surface irradiated by SR was etched with the depth of 160 Å. Thus, the each rate was estimated to be 0.16 Å/mA·min which is almost the same to those for the etchants of O_2 and NO_2 in the pressure of 0.1 torr. However, the etch rate in the former case is quite high comparing with those in the latter case, if the difference of the pressure in both cases is considered. This also indicates that oxygen radicals play an essential role on etching the diamond surface.

We would like to thank to Prof. M. Kamada for his valuable discussion on our experiment. The project was supported by a Grand-in-Aid from the Japanese Ministry of Education, Science, and Culture, for Scientific Research, No.09450021.

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Table 1. Comparison of etch rates of diamond between the different etchant gases

Etchant	Etch rate(Å/mA·min)
O_2(0.1torr)	0.13
NO_2(0.1torr)	0.15
H_2O(0.1torr)	0.08

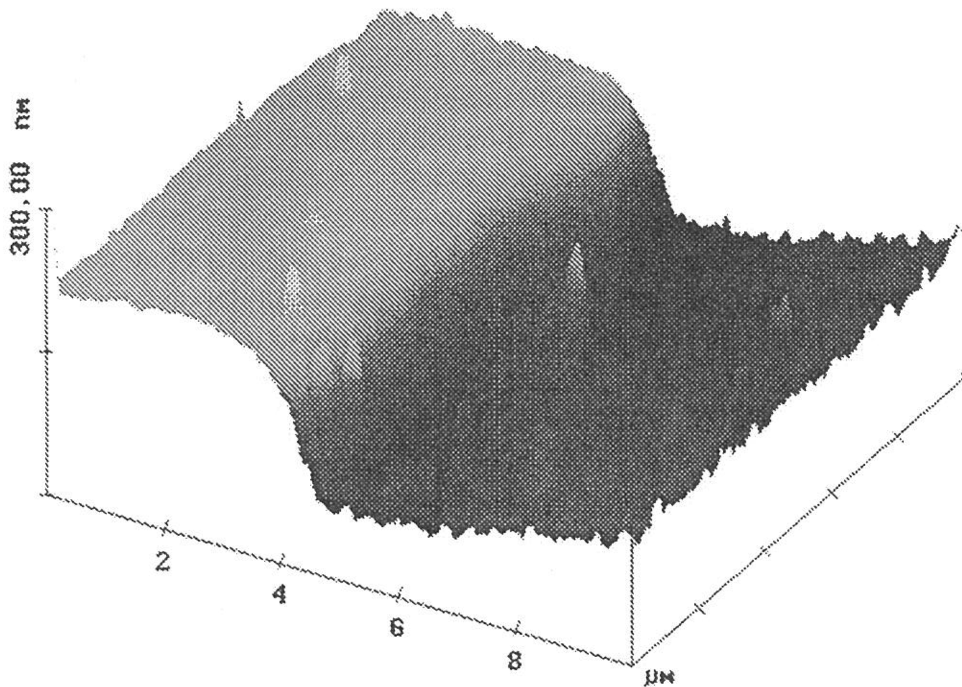

Fig.1. AFM micrograph of the diamond surface etched in the atmosphere of atomic oxygen generated by a microwave radical source. The depth of the etched surface was 16 nm. The dose of SR was 10,000 mA·min and the temperature of the surface on etching was 80℃.

(BL8A)

UVSOR Excited CF_4 Plasma Etching of Si Wafer Through LB Resist Film

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Introduction

In the series of UVSOR excited CF_4 plasma etching of silicon wafer, 50 nm line and space (L&S) pattern etching was realized in the previous work using a commercial resist SAL-601 (Shipley Far East Ltd), which is a negative tone chemically amplified resist [1]. However, this resist was developed for 100 nm pattern fabrication. Therefore, there is a need of a new resist for finer pattern fabrication. As an example of fine pattern fabrication resist, a fatty acid Langmuir Blodgett (LB) resist film was selected for the present experiments. It is reported earlier for LB resist films of PMMA that the these films show very low pin hole density of 10 cm^{-2} as compared to the conventional spin coated films of same thickness, which is more than 10^4 cm^{-2} [2]. It must be noted here that the proximity effect forces the use of resist film with thickness of same order of magnitude as that of the pattern dimension. In this respect also it is important to explore the suitability of LB resist films for fine pattern fabrication.

However, one problem of using LB resist film for fine pattern fabrication is the plasma etching resistivity of the LB resist films. The extreme low thickness of the films make the matter more difficult. Synchrotron Radiation Excited Plasma (SREP) is known for its low ion energy during plasma because the plasma is excited without any high electrical field. Another important aspect for this etching process is that because of the external energy source for plasma generation, the plasma parameters become independent of the gas parameters. Due to these aspects, this etching process is one of the attractive processes for nano scale pattern fabrication.

In the present work, we have continued the initial experiments of studying the etching characteristics of silicon. Further, we characterized the LB film etch rate with respect to that of silicon and finally carried out etching of fine pattern and obtained 100 nm L&S pattern successfully.

Experimental

The etching set up used for the present experiments was equipped along with beam line BL8A. Due to the requirement of high pressure during etching, the set up was arranged so that the maximum volume of gas is pumped through the rotary pump. The rotary pump used here was having pumping speed of 50 l/min. The CF_4 gas flow was controlled using a needle valve, and measured using a mass flow meter. In order to keep continuity with the earlier experiments [1], the gas pressure throughout the present experiments was kept constant at 130 mTorr. The CF_4 gas flow rate to maintain this pressure, was in the range of 60 sccm. The samples were arranged perpendicular to the incident radiation with the help of a micromanipulator, while being biased to −196 V with the help of a battery. We have earlier found that for CF_4 gas, the etching can be realized under negative bias voltage [1].

The etching experiments were done at a constant current of about 190 mA, and the dose was varied from 500 mA.min to 2500 mA.min. The samples were prepared by first coating 20 monolayers of stearic acid ($CH_3(CH_2)_{16}COOH$) on (100) oriented silicon samples using LB technique, followed by electron beam patterning at 50 kV with a dose of 5000 $\mu C/cm^2$. Two types of patterns were made. One was used for measuring the thickness of the patterns before and after etching. Because we used surface recorder for this purpose, these

were big dimension L&S patterns having width of 5μm and length 4mm. These samples were exposed to varying dose as mentioned above. The other pattern was a fine pattern with different L&S patterns from 25 nm to 5 μm width and was exposed to a dose of 2000 mA.min.

Results and Discussion

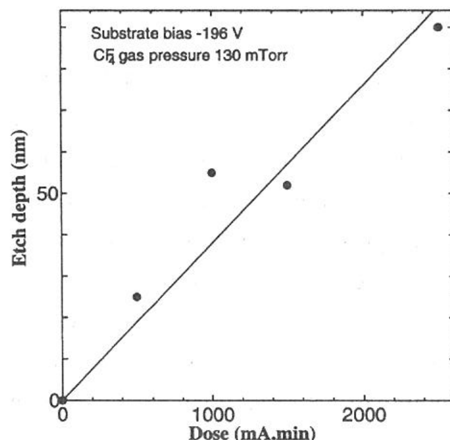

Fig. 1 :Etch depth dependence on dose

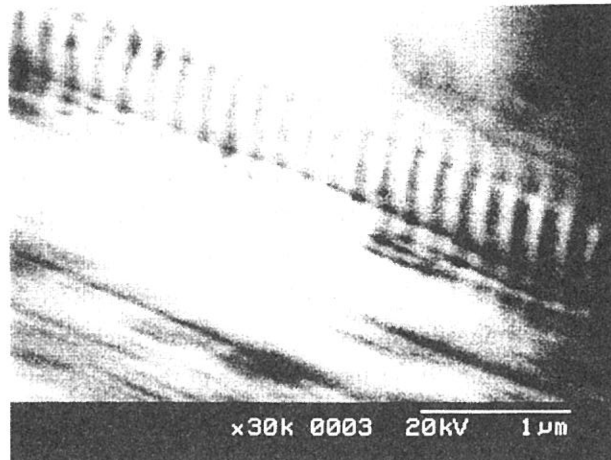

Fig 2. : SEM micrograph showing etched fine pattern

Figure 1 shows the recorded etch depth against the dose for the given experimental conditions. The etch depth obtained here for 2500 mA.min is found to be about an order lower than that obtained earlier [1] at about the same, -200 V substrate bias. This result is attributed to the possible difference in the gas flow rates, and thus the difference in the effective concentration of the etching species, as the pumping arrangement is different. Because in the present experiments a rotary pump has been used as compared to earlier, when a turbo molecular pump was used which has much higher pumping speed, the flow rates in the present experiments could be much lower. As developed and as etched 5 μm pattern were measured for their thickness using the surface recorder and the etch rate ratio of silicon and LB resist film was measured. It was found for all the dose conditions that the average etch rate ratio is 1. This may be either due to improper exposure of LB films while patterning or due to unsustainable ion energy during etching. All the patterns were found to be over etched. However, even at this etching ratio, fine patterns could be successfully transferred into silicon. Figure 2 shows the SEM micrograph of 100 nm L&S pattern after etching. Due to low height of the etched pattern, there was a considerable difficulty in obtaining an SEM micrograph. The present picture has been recorded at a an viewing angle close to 90°, and hence, a very small portion in the picture is actually focused.

Conclusions

Here we have conducted an initial study of silicon etching in SREP using extremely thin LB stearic acid resist films. A fine pattern of 100 nm L&S could be successfully transferred into silicon. However, it is found that the etch rate ratio between silicon and the LB resist film is only 1:1. Further optimization of the LB films preparation process and lowering of substrate bias is necessary to improve this etch rate ratio.

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(BL8A)

Velocity Distributions of the Desorbed Neutral Species Formed from the Ablation of Synchrotron Radiation-Excited Teflon

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Introduction A large body of information has been obtained for the state distributions of the ionic species formed from synchrotron radiation(SR) excited molecules and surfaces. However, detection of the neutral desorbed species formed in SR-excited processes has been rarely done, mainly due to the experimental difficulties in detecting neutral species. Y. Zhang, et al.[1] have found that the Teflon (commercial name for polytetrafluoroethylene, PTFE), $(-CF_2-)_n$ is quite easily ablated by irradiating SR upon it and Inayoshi et al.[2] have found that desorbed species formed by ablation of SR-excited Teflon can form Teflon-like thin films. Despite these findings the mechanisms of the SR-excited ablation of Teflon were not understood nor what kind of species are desorbed in the ablation process. The combination technique of GC/MS (gas chromatography /mass spectrometry) has been applied to determine the decomposition product from the pyrolysis of Teflon and it has been found that the major decomposition product formed at 750℃ is tetrafluoroethylene (TFE). Therefore from the thermal decomposition TFE moieties are chopped off from the end of the polymer chain. In the present project we have measured the velocity distributions of the desorbed neutral species formed from the ablation of SR-excited Teflon, to understand what species are formed in the ablation process and what mechanisms are applicable for the very fast ablation of Teflon.

Experimental The apparatus used for the present study was constructed for the measurement of the time-of-flight (TOF) spectra of the SR-excited surface reaction processes[3]. The TOF spectra of the desorbed species are measured using electron bombardment ionization mass spectrometry combined with a pseudo-random correlation chopper technique. The distance from the chopper to the ionization region was 31.1 cm. A TOF spectrum was measured as a function of the neutral flight time from the chopper to the ionizer region. The "white" focused SR was used for the experiment. The deflection angle of the focused light due to the Pt-coated mirror was 4 degrees. The intensity of the SR was adjusted using a filter made of layered Ni meshes and its intensity was monitored by photoelectric current (PEC) measurement.

Results and Discussion The TOF spectra were recorded at about 60 ion masses from *m*/e = 19 up to about 400. It is well known that organohalogen compounds are easily fragmented upon electron bombardment and thus daughter ions with masses much lower than the neutral mass are usually detected. The typical TOF spectra observed at masses, *m*/e = 19(F^+), 31(CF^+), 50(CF_2^+), 100($C_2F_4^+$), 129, and 382 are shown in **Figure 1**. The species arriving at the ionizer at earlier times have higher speeds. The TOF spectral profiles are not identical, which means that, for example, the neutral species detected at mass *m*/e = 19 (F^+) mostly originate from lighter species, such as F atoms as well as C_2F_4. To extract more information out of the spectra each TOF spectrum was analyzed assuming that it is a superposition of two or three velocity components, since none of them could be fitted to a single Maxwell-Boltzmann (MB) distribution. The MB distribution is characterized by a ratio, M/T, where M and T are the mass and a translational temperature of the desorbed neutral species. The translational temperature of the molecules desorbed from the surface by thermal desorption is known to be equal to the surface temperature, T_s. Thus the surface temperature was assumed to be equal to the translational temperature (T) of the Kr atom scattered to the direction normal to the surface when the effusive Kr beam was collided to the surface at an incident angle of about 45 degrees. T_s determined in this manner was adopted even when the SR is shone on the surface: T_s goes up when the SR is shone on it. In order to control the substrate temperature the Teflon plate was heated with a ceramic heater attached from the rear side.

Most of the data are fairly well fitted with two velocity components. Once the ratio, M/T, is determined from the fit the mass of the neutral species can be determined since T is set to be equal to T_s. However, there is one exception; for F atom desorption T for the fast component was found to be somewhat higher than T_s, especially when the light intensity was high. **Figure 2** illustrates T for the F atoms detected at mass *m*/e = 19 as a function of irradiation time on the same sample spot. The surface temperature was T_s = 405 K. One sees that

T is higher than the T_s by about 30% at the start of the irradiation. The F atoms formed are repulsed from the surface on a repulsive surface. **Figure 3** shows the neutral mass determined for the slower component detected at mass m/e = 19 and for T_s = 405 K as a function of irradiation time. The determined mass is almost equal to the mass number corresponding to a light molecule C_2F_3 or C_2F_4.

It is noted that the intensity of the desorption product is very low when the light intensity is very low (in the single bunch operation) and the surface temperature is kept low. After the irradiation under this condition the color of the sample surface turns light brown. Therefore it is concluded that the ablation does not proceed at a noticeable rate as long as the surface temperature is low and thus the sample was heated from the rear side to induce desorption. There is a tendency that heavier species are desorbed as the surface temperature is increased. **Figure 4** shows the masses of the desorbed species as a function of SR intensity and substrate temperature. The highest mass determined amounts to 833 amu. It is speculated that cleavages of C−F and C−C bonds are induced by inner core excitation of the constituent atoms followed by Auger processes and desorption of the imbedded fragments occurs after their diffusion to the surface by thermal motion. Although not shown here, the apparent desorption rate follows an Arrhenius rate form $k_{des}(T) = A\exp(-E_a/kT)$, implying the above mentioned notion.

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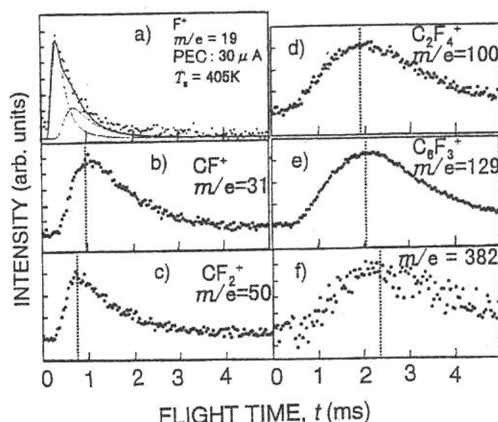

Figure 1. Typical TOF spectra of desorbed species detected at ion masses m/e = a) 19(F^+), b) 31(CF^+), c) 50(CF_2^+), d) 100 ($C_2F_4^+$), e) 129, and f) 382.

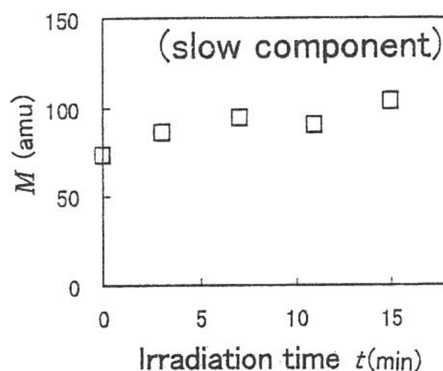

Figure 3. Irradiation time dependence of the translational temperature T for the slow component detected at F^+(m/e = 19) and at T_s = 405 K.

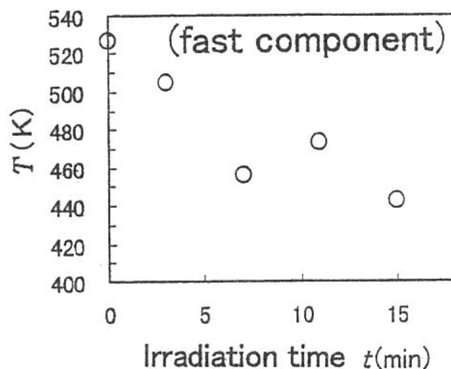

Figure 2. Irradiation time-dependence of the translational temperature T of F atoms (fast component) detected at F^+(m/e = 19).

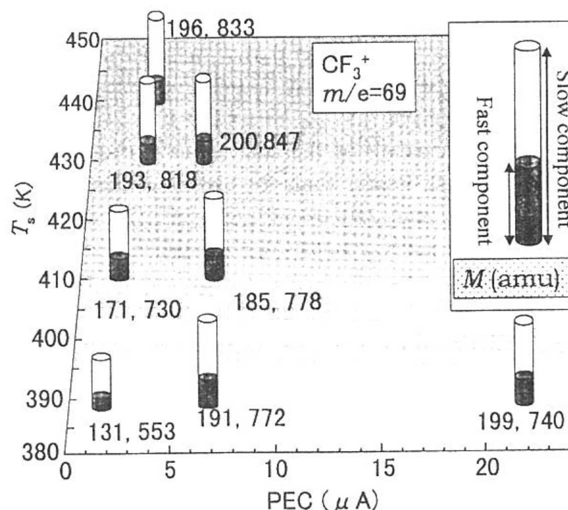

Figure 4. Surface temperature (T_s) and light intensity (measured by PEC) dependence of the mass of the desorbed species detected at mass m/e = 69 (CF_3^+). The height of the rod represents the molecular weight. The mass numbers are also indicated in the

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Fabrication of Fluorinated Thin Films by SR ablation

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Introduction:

Teflon material is expected to use for the micro-machine fabrication. So far, we have successfully deposited Teflon materialssuch as PTFE, FEP and PFA and fabricated 19É m size pattern on them anisotropically at a high speed by using SR[1]. However, it has not been reported that the fine pattern of Teflon was fabricated on the curved surface to use this process further for maicro-machining.

In this study, we have formed $(CF_2)n$ films on the curved surface by using CF_2 radicals and fabricated them by SR ablation. Moreover, we have fabricated the metal fluoride thin films which was evaporated with electron-gun. On the basis of these results, we have proposed the total dry process of fabrication of fluorinated materials using SR.

Experiment and results:

The experiments were performed in BL-8A line in UVSOR.

CF_2 radicals which were considered as a precursor for the Teflon material were formed by the pyrolytic decomposition of HFPO gas. The $(CF_2)n$ thin films of 1.5 μm thickness were formed on 1/8 inch stainless tube and nichromium wire(0.5mm ϕ) by using the CF_2 radicals. The mesh mask was set on these samples and irradiated by SR at 10^{-4} Pa in vacuum and a room temperature.

Figure 1 shows the SEM images. The fine patterns were found to be fabricated on Teflon films deposited on the curved surface. In order to investigate the reaction mechanism of Teflon with SR, the wavelength irradiated on the Teflon surface is selected with the carbon and MgF_2/Carbon masks and thereby the ablation rate of films is evaluated.These results obtained are under analysis.

Furthermore, we have investigated the fabrication on the metal films as well as Teflon. AgF, MgF_2 and AlF_3 thin film of 50nm thickness were formed on Si substrate. These samples were irradiated through the mesh mask at 10^{-4}Pa in vacuum and a room temperature. We have successfully formed fine patterns on all films of AgF, MgF_2 and AlF_3 .

Figure 2 shows SEM image of 77 μm square patterns. Figure 3 shows the SR intensity dependence of etching rate. It was found that the etching rate increased linearly with increase of SR current and the etching rate was dependent on the materials which will be due to the evaporated pressure and SR absorption rate of materials.

Figure 4 shows SR duration dependence of etching rate. The etching rate was decreased as the SR duration was increased. The irradiated surface of AlF_3 pattern was investigated by XPS.

Figure 5 shows F/Al ratio of surface of films under-patterned by SR.The change of ratio was corresponding to the pattern area with and without SR irradiation. These results indicate the reaction mechanism where fluorine atoms were desorbed fast from metal fluoride surface by SR irradiation and the film structure is changed from fluoride rich surface to metal rich one with SR duration. Therefore, the etching rate is decreased with SR duration.

Summary:

The fine pattern fabrication of Teflon on the curved surface using SR was investigated for micro-machining process. The novel dry process using SR, where the $(CF_2)n$ films were formed on the curved surface of wire by using CF_2 radicals generated from pyrolytic decomposition and SR was irradiated on them through a mesh, was successfully demonstrated.

Furthermore, the fine pattern fabrication was investigated on metal fluoride films of AgF, MgF_2 and AlF_3 by using the dry process, where metal fluoride films were evaporated by electron gun and SR was irradiated on the films. We found the metal fluoride patterns were successfully fabricated by the SR dry process. The reaction mechanism of the ablation of fluoride films with SR irradiation was proposed.

[1]M.Inayoshi et.al.,Jpn.J.Appl.Phys.Vol.34,Pt.2,No.12B,pp.L1675-L1677,December 1995

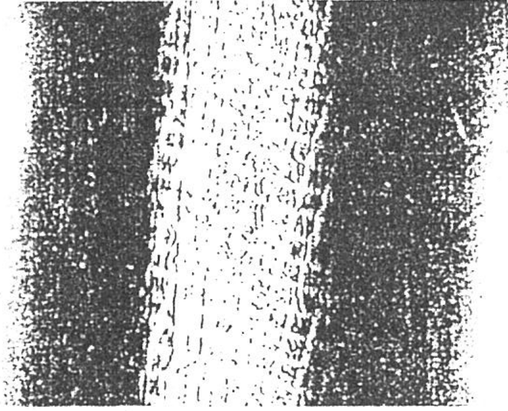


Figure 1:SEM photograph of the fine patterns created in Teflon film deposited on the curved surface

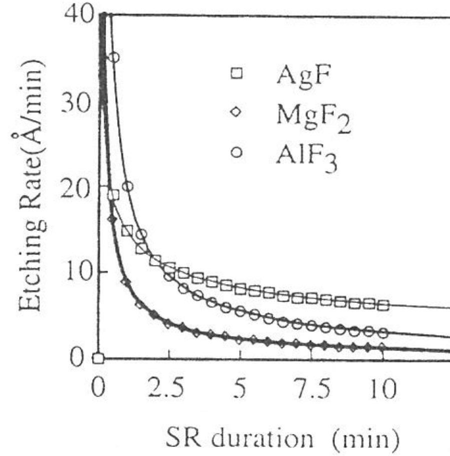
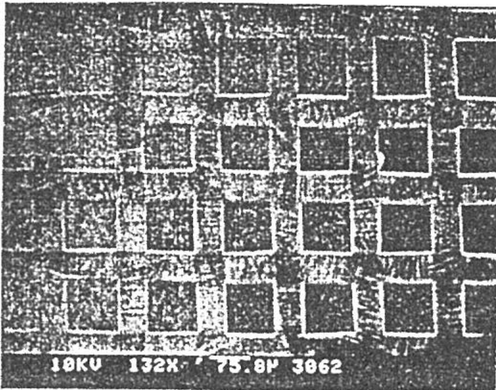


Figure 4:Etching rate of AgF,MgF2,AlF3 as a function of SR duration



Figurre 2:SEM photograph of the fine 77μm square patterns created in MgF_2 film

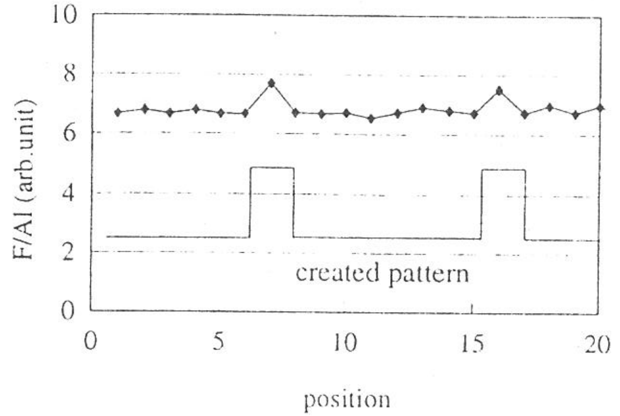


Figure 5:F/Al ratio of surface of films under-patterned by SR

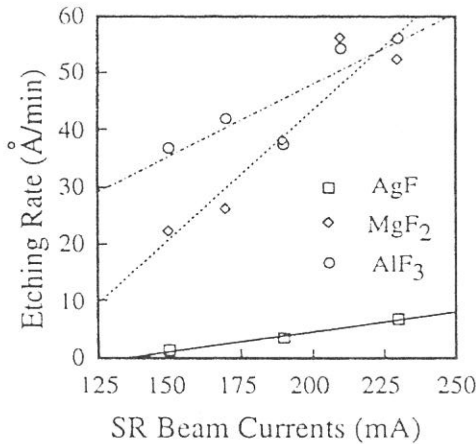


Figure 3:Etching rate of AgF,MgF2,AlF3 as a function of SR current