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Application of Synchrotron Radiation to Microfabrication

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We tried to apply synchrotron radiation to microprocesses for microsystem engineering. Deep depth Xray lithography have been performed using X-rays in New SUBARU (1.5GeV). We controlled the shapes of inclined sidewall patterns by using round absorber of X-ray mask and demonstrated quasi-3D microfabrication. Vacuum ultra violet region of SR is suitable for inducing photochemical reaction. As one of the application to semiconductor process, crystal film growth was attempted on Si substrates. It is demonstrated that the homo epitaxial temperature is lowered to 40℃. Furthermore we found that high selectivity was attained in SR-excited photochemical film growth.
Key words: shynchrotron radiation, microfabrication, LIGA, photochemical reaction, microsystem

1. INTRODUCTION

Synchrotron radiation (SR) is a potentially novel and powerful light source of x-rays and vacuum ultraviolet for microfabrication, since SR has many advantages such as high brilliance, high photon energy above ionized potential and excellent directivity as a light source for material excitation. Interaction of high energy photons with gases, surfaces, adsorbates and solids is significant compared with other light sources and this plays an important role in photochemical reaction. In recent years, several unique features have appeared in several kinds of microprocess such as SR-excited etching, film deposition, doping , surface/bulk modification and deep depth x-ray lithography. These process properties are distinguished by their high selectivity of materials, low temperature, high reaction controllability and nano-level accuracy. This paper reports our results of SR application to several fields of microfabirication like structure fabrication, synthesis and modification of materials and demonstrates these advantages as a new photo processings.

1. MICROSTRUCTURE FABRICATION

1.1 LIGA process for quasi 3D fabrication

Needs of the microstructures with height of over a few hundreds micron have been increased in the various micro electro mechanical systems (MEMS) fields such as high power microactuators, high sensitivity micro sensors and microprobe spectroscopy for nano technology. Thus microstructures with high aspect ratio add new functions and increase the performance of the MEMS. In order to fabricate high aspect ratio microstructures LIGA (Lithographie, Galvanoformung and Abformung) process using synchrotron radiation is one of the most promising techniques. Although conventional LIGA is suitable for forming high aspect ratio microstructures, fabrication flexibility in vertical-direction shape is very restricted. So far, several methods to achieve quasi-3D microstructures have been attempted[1], however, technique effective for mass production with fabrication flexibility is not realized. There are two approaches to attain quasi 3D resist patterns in LIGA; one is to give the gradual intensity distribution to the x-rays transmitted from the mask using absorbers with thickness variation in tangential direction, and the other is to form accumulated exposure energy distributions in sagittal direction by exposure time control by mask moving. Although the former way is decided by x-ray absorber shape and material, it is better for mass production since less exposure steps and time and has flexibility of fabricated pattern structure. We prefered former way. Furthermore we control the intensity distribution of cross sectional SR beam to add graded depth distribution of resist patterns over entire exposure field. The beamline for LIGA[2] in New SUBARU (1.5GeV), which has two x-ray mirrors is designed to obtain high SR beam intensity over the energy range from 4 keV to 6 keV. We attempted to form inclined sidewall patterns using SUS wire mesh as a exposure mask. Wire is chosen since its circle cross section brings abrupt x-ray absorption distribution effective for inclined shape patterns. Graded depth variation of the patterns over entire exposure field is added by obtaining gaussian-like cross sectional intensity distribution of SR using mirror-bending system of the beamline. Figure 1 shows SEM photograph of the quasi-3D PMMA microstructure. X-ray dose is 3000 mA.min. As shown clearly inclined shape sidewall and graded depth of resist patterns were successfully fabricated. Highest depth of the patterns is 70μm. This demonstrates the possibility of the high throughput quasi 3-dimentional microstructure fabrications.

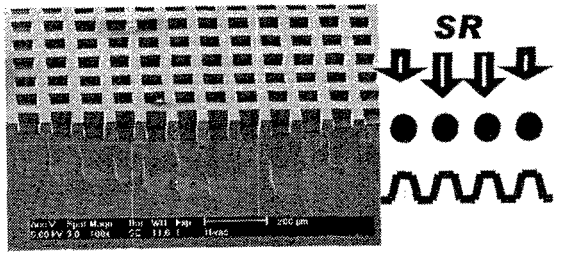

Fig.1 Scanning electron microscope image of the quasi 3-dimentional PMMA microstructure.

1.2 Spatial Period Division

Submicrometer or less periodic structure are fundamentally important for a number of areas, such as planar superlattice electron devices, distributed feedback lasers, graphoepitaxy, and X-ray optical devices. To improve the electrical or optical properties of such devices, it is necessary to obtain precise and finer periodic structures over larger areas. Spatial periodic division (SPD) is a lithographic technique in which the patterns of a 1/n spatial period of a parent mask are exposed on a resist film by near field diffraction from the mask. [3]

Although this method has many advantages, there is a serious disadvantage in that diffracted field intensity distribution is easy to vary over the exposed area in the lithographic technique. This is caused by the fact that the intensity distribution is strongly dependent on the size of the gap between the parent mask and the wafer. We controlled the SR bandwidth to nearly the optimum width by using a W/Be multilayer mirror fabricated by an atomic sputter deposition method. Figure 2 shows

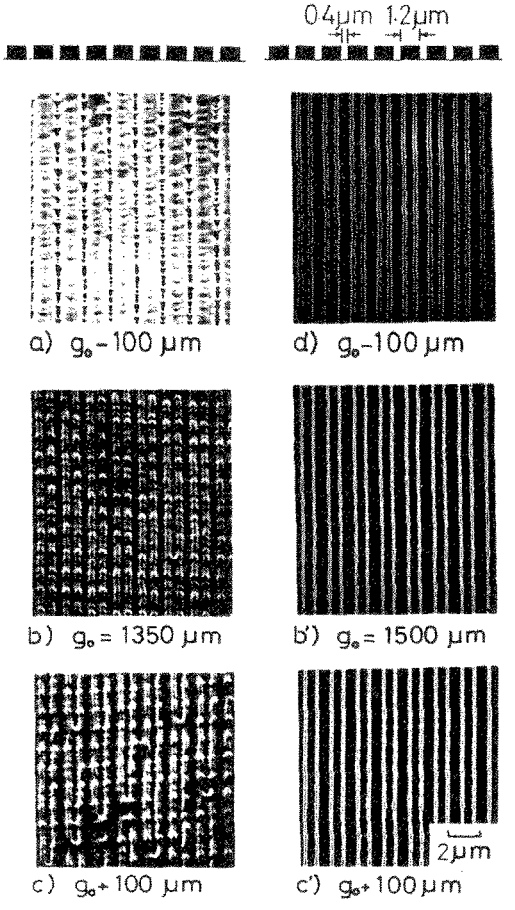

Fig.2 SEM images of SPD patterns. Cross-sectional structures of the parent mask are given upward.

scanning electron microscope images of resist patterns fabricated by the SPD technique with gaps of near the optimum gap g_0. Cross sectional structures of the parent mask also re shown at the top of this figure 2. Patterns (a), (b) and (c) were fabricated without SR bandwidth control by multilayer mirror. The patterns had many disturbances and the linewidths and heights are not uniform over the exposed area. This is mainly due to the excessively wide bandwith of the source light. On the other hand, patterns (a'), (b') and (c') were fabricated with SR bandwidth control. Pattern quality clearly improved with bandwidth control. Thus uniform 0.2 μm SPD patterns were obtained, and it was demonstrated that SR bandwidth control of the SPD by X-ray optics effectively reduced disturbances and pattern deterioration .

2 MATERIAL SYNTHESIS

2.1 Si photo-epitaxy at Room Temperature

Low-temperature and low-damage semiconductor processes have recently become more important for future nanometer- devices such as quantum effect devices or superlattice devices. Photo-excited epitaxial growth is one of the leading candidate for such processes and has been widely investigated[5]-[6]. The photon energies of light sources generally used in these studies, however, lie below the ionization potential of most reaction gases. This means that the possible photo-excited reactions are greatly restricted. Whereas, the photon energies of SR are suitable for inducing core or valence excitations of reaction gases and solids, which lead to non-thermal reactions such as direct photolysis of gas molecules into active species or stimulated desorption of adsorbed atoms. This may be useful not only for lowering the temperature of epitaxial growth but also for examining growth kinetics, since SR irradiation does not induce photothermal reactions. In addition to these advantages, continuously tunable photon energy and excellent directionality enable fine control of the surface reactions and high-resolution area and material selective reactions. The primary intent of this section is to clarify the characteristics of SR-excited Si epitaxy using disilane in some practical applications of semiconductor processes such as selective growth and doping.

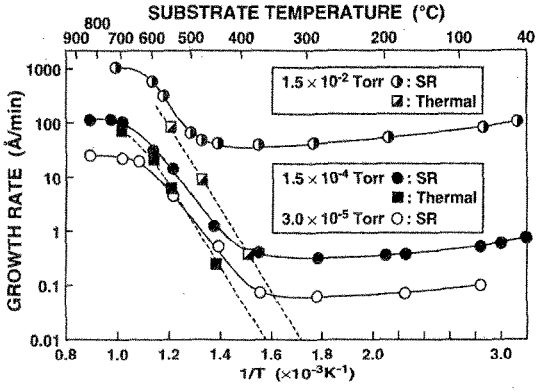

Fig.3 Growth rate of epitaxial Si films as a function of Si substrate temperature. Disilane pressures were $1.5x10^{-2}$, $1.5x10^{-4}$, and $3.0x10^{-5}$ Torr respectively.

Figure3 shows a typical temperature dependence of the growth rate in SR-excited Si epitaxy using disilane. The growth rate for thermal deposition without SR irradiation is also shown in the figure (broken lines) for comparison. As can be seen in the figure, the dependence can be separated into three regions since the reaction mechanism changes with the temperature :above 700℃; from 350 to 700℃; and below 350℃[7]. Above 700℃, the effect of SR irradiation on growth rate are not observed. The activation energy of this region is 7.5 kcal/mol, which is close to the activation energy of disilane dissociative adsorption 6.3 kcal/mol. At temperatures from 700 to 350℃ where hydrogen desorption is considered to be rate limiting, the temperature dependence of the growth rate is steep and a RHEED 2x1 surface reconstruction pattern is observed. For SR-excited growth, the activation energy in this region is 36 Kcal/mol and for thermal growth, it is 48 Kcal/mol. In this region, the enhancement of growth rate due to SR irradiation becomes more clear as the temperature decreases. In this region, it is interpreted that the growth reaction is the sum of the photo process and the thermal process. In comparison, below 350 ℃, where the growth rate depends less on the substrate temperature and increases gradually as temperature decreases, growth proceeds mainly by photo chemical

reaction. To derive more detailed information about the fundamental mechanism involved in SR excited growth, the tangential distribution of growth rates for Si grown films was examined. Figure 4 (a)-(d) shows the profiles for grown films at various disilane pressures with perpendicular SR incidence. The temperature is 60℃, where thermal growth is negligible. The FWHM of beam was 3.5 mm. At pressures above $7.0x10^{-5}$ torr, it is noteworthy that profile exhibits a broader bottom than the beam intensity profile, which indicates that the deposition occurs by a combination of surface or near surface excitation and gas-phase excitation. The solid line in the figure shows the contribution of the gas-phase excitation calculated assuming a model in which the active species

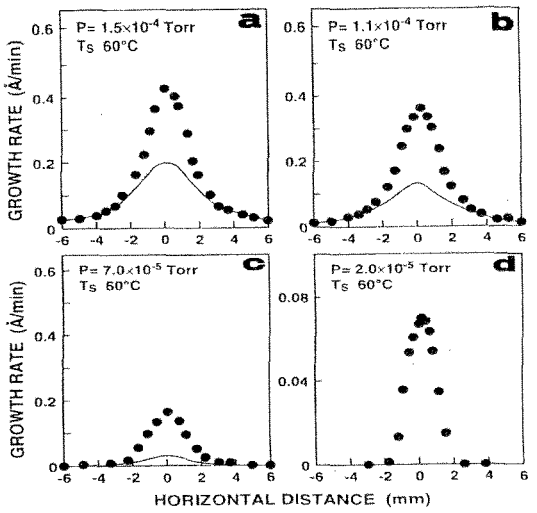

Fig.4 Growth rate distributions on Si substrate as a function of disilane pressure.

generated in the SR beam path did not undergo any collisions before reaching the substrate. At the pressures shown in Fig. 4, the mean free path of the disilane molecules is more than 100 cm, and therefore active species reach the substrate surface without any collision. As can be seen in the figure, the gas-phase contribution decreases as the disilane pressure decreases. In SR excited epitaxy using disilane, three species are electrically excited by SR: gaseous disilane as described; disilane molecules weakly trapped on the surface; and irreversibly chemisorbed surface Si hydride. The contribution to growth resulting from the excitation of surface hydride can be isolated at low disilane pressures less than $3x10^{-5}$ Torr, where the photo dissociation of gas molecules is negligible. The growth rate saturated below $3x10^{-5}$ Torr, which shows the contribution from the excitation of the adsorbed Si hydride.The contribution to growth rate from gas molecules,which shows no dependence on the temperature can be derived theoretically as shown in Fig.4. This contribution can also be estimated using SR incident parallel to the substrate. The SR beam does not contact the substrate, it only excites the gas above the substrate surface. The temperature dependence of the growth rate at parallel incidence were also investigated. It is notable that the growth pathway due to photolysis of gas molecules shows no temperature dependence. The contribution from the photoexcitation of weakly trapped disilane is then evaluated using SR incident perpendicular to the substrate and subtracting the theoretical gas phase contribution(Fig.4) and the contribution from the excitation of the adsorbed Si hydride. At $1.5x10^{-4}$ Torr disilane, the contribution from this weakly trapped disilane is about 40 %. This contribution decreases as the disilane pressure decreases and finally vanishes below $3x10^{-5}$ Torr.

We tried Si photoepitaxy at near room temperature with $3x10^{-5}$ Torr where epitaxy proceeds only by the excitation of adsorbed Si hydride. Figure. 5 (a) shows the RHEED image of the as deposition film and shows that epitaxy at 40 ℃ is successfully achieved. Fig.5 (b) shows the RHEED of the film annealed at 500 ℃ for 5 minutes, above which adsorbed hydrogen was thermally desorped. Cross sectional TEM image of the film shows that epitaxial film was successfully gown even at the interface of the substrates[8].

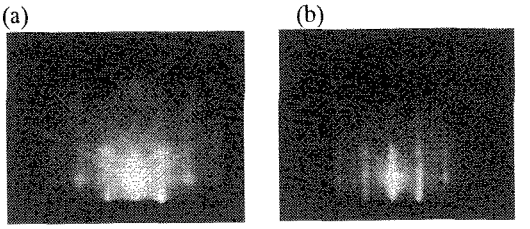

Fig.5 RHEED images of the Si photo-epitaxial film at 40 ℃(a) as depositon film. (b)after annealed at 500 ℃

The effect of SR irradiation on the crystallinity of the epitaxial Si film was also investigated using RHEED observation on the irradiated and non-irradiated area on the grown sample surfaces[9]. It was found that the irradiated area shows better crystallinity than the non irradiated area over the temperature range from 340 to 500℃. The increase of the surface temperature due to SR irradiation is evaluated to be less than 20 ℃, this phenomenon is considered to be caused mainly by the photo-excitation effects. The concentrations of contaminants included in the film for irradiated and non-irradiated areas were also compared by means of secondary ion mass spectroscopy measurements. It was found that there was no change in the oxygen or carbon concentrations in eitherarea. This proves that irradiation of SR does not increas ethe incorporation of contaminants.

2.2 Perfect selective epitaxial growth

The selective epitaxial growth (SEG) of Si on Si/SiO_2 substrates by gas-source MBE has been widely studied [10], since it allows selective epitaxial films with few surface defects to be fabricated at low temperatures with high thickness controllability. This is one of the most promising techniques for the fabrication of fine self aligned structures in high-speed Si devices. However, SEG through gas-source MBE using silane or disilane has so far been unsatisfactory in the sense that, even if SEG occurs during the initial stage, it eventually breaks down after an incubation period, after which a poly crystalline Si film forms on the SiO_2 surface. This problem arises mainly because the nucleation and coalescence of Si clusters on the SiO_2 cannot be completely suppressed in conventional gas-source MBE, where selectivity relies solely on the finite difference in the decomposition probability of silane or disilane between the Si and SiO_2 surfaces. To attain perfect selectivity with an infinite incubation period, the SiO_2 surface must either be modified to prevent Si nucleation, or the Si nuclei that form on it must somehow be removed to prevent the growth of a continuous poly-Si film. In

this work we employed SR to induce chemical reactions to remove the nuclei. Silicon (100) substrates covered partially with thermally grown SiO_2 patterns were used for selective growth. Prior to epitaxial Si film growth, the native oxide on the surface of the Si windows was removed by heating the substrate to 980℃ for 10min. Disilane gas was fed into the reaction chamber while an SR beam perpendicularly irradiated the sample surface. It is confirmed that no Si deposition occurred on the SiO_2 patterns after SEG with SR irradiation, while epitaxial Si films with [113] facets on their edges grew on the Si windows. AES spectra of the SiO_2 surface (Fig.6 (a)) show that without SR irradiation the Si(LVV) peak at 92 eV appears as a result of Si nucleation and ensuing poly-Si film formation on SiO2 when the growth time exceeds 40 min. The emergence of the Si peak also corresponds to a change in the RHEED pattern from a halo to a ring. With SR irradiation, the Si peak does not appear even after 800 min (Fig.6 (b))[11]. We also confirm that selectivity could be maintained for as long as the SiO_2 films existed on the substrates. This is a highly distinctive feature of SRSEG which has not yet been observed in conventional SEG by gas-source MBE

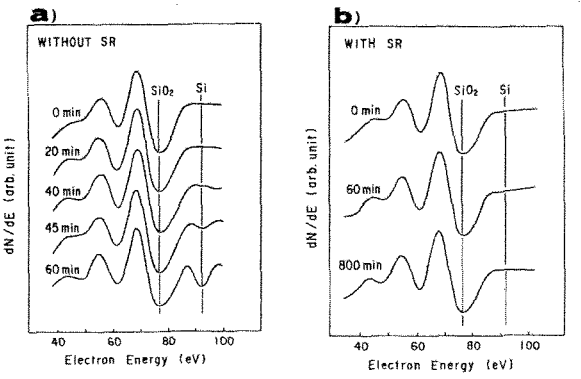

Fig.6 Time dependence of Auger spectra of SiO_2 surfaces obtained after SEG without SR (a) and with SR(b). Surface temperature was 750℃ and the disilane pressure was $3x10^{-5}$ Torr.

3 STRUCTURE CONTROL OF MATERIALS

3.1 Modification of the composition of Mo oxide film

Irradiation effect of soft x-rays and vacuum ultraviolet light for several material surfaces have been studied using several methods. Especially, photostimulated desorption of oxygen from a metal or metal oxide surface has beeen widely investigated, however, they have focused on the chemisorbed species desorption or top layer atoms desorption. Desorption at the near surface and bulk stoichiometry have not almost investigated. Nagase and Utsumi et.al. reported the remarkable stoichiometric changes in the near surface and the bulk of molybdenum oxide induced by SR irradiation. We compared x-ray diffraction patterns of 60 nm-thick molybdenum oxide films before and after SR irradiation (9A.min at 500 ℃). After prolonged SR irradiation, x-ray diffraction peaks of MoO_2 appear, whereas those of MoO_3 disappear completely. This suggests that photo stimulated desorption of oxygen by SR depends strongly on the bonding state or the site of oxygen atoms. The Mo-O bonds in MoO_3 are more easy to to dissociation than those in MoO_2[12].

Not only at the bulk, structure changes have been reported at also surfaces. Akazawa observed that SR irradiation selectively desorp hydrogen from the self-limitted adsorbed mono and di silicon hidryde on the Si(100) surfaces using time of flight mass spectroscopy [13]. From the point of the practical application, SR can change the material structure without braking the crystal structure or surface adsorption configration. This remarkable feature of SR as a fabrication tool leads to the atomic level process and new material synthesization.

4 SUMMARY

Deep depth X-ray lithography have been performed using X-rays ranging from 2 keV to 10 KeV of NewSUBARU. We controlled the shapes of inclined sidewall patterns by using round absorber of X-ray mask and demonstrated quasi-3D microfabrication. Furthermore depth of the PMMA pattern was controlled gradually by using SR beam which has tangential intensity distribution. As one of the application to material synthesization, epitaxial Si films are grown on Si substrates by photo-excited gas-source MBE sing disilane. It is demonstrated that the epitaxial temperature is lowered to 40℃. And perfect selective epitaxial growth between Si/SiO_2 substrates can be achieved irrespective of growth time at temperatures above 700℃. Furthermore the composition of metal oxide film was successfully changed keeping the stoichimetry and crystallinity of the film by photomodification.

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