

Tuesday Evening Poster Sessions, November 4, 2003

Plasma Science and Technology

Room Hall A-C - Session PS-TuP

Poster Session

PS-TuP1 Silicon Dioxide Etching Processes Employing Electron Beam Excited Plasmas, *M. Ito, K. Takeda, Y. Tomekawa, M. Iwakaki, T. Shiina, Y. Okamura*, Wakayama University, Japan; *M. Hori, T. Goto*, Nagoya University, Japan

Optical devices or micro total analysis system fabricated by using micromachining techniques attract much attention because of their usefulness. In the fabrication processes, micromachinings of non-planer thick dielectric materials such as optical fibers and thick quartz parts are necessary. In such processes, the fast atomic beam etching and ion beam etching are employed because the RF self-biasing in the conventional reactive ion etching (RIE) is not applicable to non-planer dielectric materials such as silicon dioxide (SiO_2). However, the etch rates of these processes are typically around few tens nm/min, which are very low compared with the RIE and so the higher etch rate is strongly required to reduce the processing time. Therefore, the biasing effect is necessary to etch the SiO_2 . On the other hand, an electron beam excited plasma (EBEP) has an excellent potential for applying self-bias to the non-planer dielectrics by using the electron beam. The SiO_2 etching characteristics using EBEP have been never reported although the SiO_2 etching is useful for the devices using micromachining techniques. Therefore, we have demonstrated the SiO_2 etching processes using self-biasing induced by an electron beam of the EBEP without any additional bias power supply. As a source gas, the CF_4 diluted by Ar (CF_4/Ar) was employed. The etch rate of 117 nm/min has been obtained. From the plasma diagnostics using a Langmuir probe and an optical emission spectroscopy, it has been found that the higher electron beam current for generating plasmas improves the plasma density and sheath potential, resulting in higher etch rate of SiO_2 . Moreover, novel pulsed EBEPs have been applied for the SiO_2 etching process. The plasma diagnostics have been carried out. These results indicated that the electron beam excited plasmas has a great potential for application to micromachining processes.

PS-TuP2 A Novel Si/SiO_2 Etching Technique for Minimizing Charge-induced Microscopic Non-uniformity in Plasma Etching, *K.H. Baek*, Samsung Electronics, South Korea; *D.H. Lee, S.J. Jung*, Sungkyunkwan University, South Korea; *C.J. Kang*, Samsung Electronics, South Korea, Korea; *G.Y. Yeom*, Sungkyunkwan University, South Korea

In this study, microscopic non-uniform etching characteristics solely caused by positive ions were investigated and a novel etching technique using energetic and directional neutrals was introduced as an alternative of reducing those charge-induced phenomena. To systematically investigate microscopic non-uniform etching characteristics, various samples designed to evaluate microscopic etching characteristics were prepared and etched in a homemade ICP (inductively coupled plasma) etching system, ion beam etching system, and neutral beam etching system. By analyzing all the results, we could clarify role of positive ions in the non-uniform etching phenomena and get an idea on reducing them. To realize the idea, we revised our previous neutral beam etching system so that it could improve flux and directionality of neutrals. By using this system, successful etching results for poly-Si and SiO_2 nearly without the charge-induced phenomena were achieved, even though the results etched in the other systems show those non-uniform etching characteristics. Thus, we recommend energetic and directional neutrals as a potential etching source for the next generation technology era.

PS-TuP3 Effects of Substrate Temperature and Ultraviolet Radiation on the Etching of Copper Films using Inductively Coupled Chlorine-based Plasmas, *K.H. Jang*, Sungkyunkwan University, South Korea; *H.R. Kim, W.J. Lee*, IMG, LG-Production Engineering Research Center; *G.Y. Yeom*, Sungkyunkwan University, South Korea

Copper (Cu) is one of the potential materials in thin film transistor liquid crystal display (TFT-LCD) because of its lower bulk resistivity and lower cost than aluminium alloy, chromium, tungsten, and nickel at room temperature. Cu etching for TFT-LCD is currently performed using wet etching methods, however, for the fabrication of high resolution display devices, the use of plasma etching process is indispensable. In reality there are several problems to be solved before Cu plasma etching to be applied to TFT-LCD processing. The main problems are the formation of involatile

etch products, lower etch rates, and high surface roughness after removing the etch products. For example, many works on Cu etching using chlorine-based plasma have been studied, however, slow etch rates and thick involatile Cu etch products remaining during the etching were reported especially for the integrated circuit (IC) manufacturing. Therefore, in this study, using an inductively coupled chlorine-based plasma, the effects of substrate temperature and ultraviolet radiation effects were investigated to obtain Cu etch rates higher than 200 nm/min and to remove the involatile etch products by changing substrate temperature and ultraviolet photon density and strength. To understand the Cu etching characteristics, we used the optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS) and measured the substrate temperature and ultraviolet intensity and wavelength. Also, a scanning electron microscope (SEM) was used to observe etched Cu electrodes profile.

PS-TuP4 The Electrical Properties of SBT Thin Films Etched in $\text{BCl}_3/\text{Cl}_2/\text{Ar}$ Plasma, *J.K. Kim, C.I. Kim, K.T. Kim, D.P. Kim*, Chung-Ang University, Korea

$\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) thin films have a lot of good features such as high resistance to polarization fatigue due to the charge-compensating role of the $(\text{Bi}_2\text{O}_7)^{2+}$. The 200-nm SBT thin films were deposited on the Pt electrode by metal organic deposition (MOD). Until now, there is no report on the etching characteristics of SBT thin films in $\text{BCl}_3/\text{Cl}_2/\text{Ar}$ inductively coupled plasma (ICP). Therefore, SBT thin films were etched in $\text{BCl}_3/\text{Cl}_2/\text{Ar}$ with using ICP etching system. The etch rates and selectivity of SBT thin films were investigated as functions of gas mixing ratio, rf power, dc-bias voltage and pressure. With adding 20% BCl_3 in Cl_2/Ar plasma, increasing rf power and dc bias voltage, and lowering pressure, the etch rate of SBT increased. The etching byproducts were investigated with using quadruple mass spectroscopy (QMS). The heterogeneous reaction of plasma on the surface of the etched SBT was investigated with x-ray photoelectron spectroscopy (XPS). The etching profiles of samples have been investigated with using scanning electron microscopy. The chemical states on the etched surface were investigated with XPS. After the etching, the electrical properties of SBT capacitors were characterized in terms of hysteresis curves, leakage current and switching polarization. After etching in $\text{BCl}_3/\text{Cl}_2/\text{Ar}$ plasma, the remanent polarization decreased and the leakage current increased. After the annealing at 600°C in an O_2 atmosphere for 10 min, the ferroelectric properties were significantly recovered. The degradation of electrical properties after the etching was considered due to the physical effect of ion bombardment and chemical residue contamination.

PS-TuP5 Modeling of Etching Mechanism of PZT in Cl_2 Plasma with the Addition of Ar, O_2 , *S.M. Koo, C.I. Kim, D.P. Kim, K.T. Kim*, Chung-Ang University, Korea

Ferroelectric Lead Zirconate Titanate ($\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$) thin films have been widely known as capacitor materials in nonvolatile ferroelectric random access memory (FRAM). The desirable properties such as high permittivity, high remnant polarization, fast switching speed, high Curie point and resistivity. Now, 32Mbit FRAM has been developed and some companies attempt to use FRAM as mobile phone memory. But the larger FRAM capacity, the smaller feature size. Therefore, in order to accomplish the integration of such devices, the etching process of PZT thin films with high etch rate, vertical etch profile, low by-product must be developed. PZT thin films were prepared on $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates by sol-gel processes. Pt top electrodes were deposited on PZT thin films by using rf magnetron sputtering. SiO_2 was deposited on Pt top electrodes. SiO_2 layer was etched in CF_4/Ar inductively coupled plasma with PR mask. We continued etching $\text{Pt}/\text{PZT}/\text{Pt}$ layer without removing PR and SiO_2 patterns. PZT thin films were etched with two steps. First, it was etched with Cl_2/Ar inductively coupled plasma, then instead of Ar, it added O_2 to Cl_2 plasma. We observed the effect of etching profile in PZT thin films during etching in Cl_2/Ar , Cl_2/O_2 plasma. The ferroelectric and electrical properties were measured with a precision workstation. We obtained stable value of remanent polarization and good fatigue resistance for PZT with SiO_2 mask as compared with Pt dot, which was used as physical mask during etching process. The structural damages to the near surface of PZT are evaluated by x-ray diffraction (XRD). The chemical deformation of etched surface was surveyed x-ray photoelectron spectroscopy (XPS).

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PS-TuP6 Etching Characteristics of LNO (LaNiO₃) Thin Films Using Inductively Coupled Plasma, C.I. Kim, J.W. Yeo, K.T. Kim, D.P. Kim, Chung-Ang University, Korea

Among the ferroelectric thin films that have been widely investigated for ferroelectric random access memory (FRAM) application, the LaNiO₃ (LNO) thin film is known to play a role to improve fatigue and imprint of ferroelectric capacitor. And LNO thin film is expected as an effective electrode for the growth of highly oriented ferroelectric thin films because it shows a pseudocubic perovskite structure ($a = 3.84 \text{ \AA}$) and an n-type metallic behavior without any doping procedure. Although, there are several advantages and Dry etching, which shows anisotropic etching properties, has become one of the critical processes for pattern transfer in ultra large scale integration, very few studies on the etch properties of LNO electrode thin films have been reported. In this study, LNO thin films were etched by BCl₃/Ar plasma with inductively coupled plasma etching system. The etch rates of LNO thin films and selectivity of LNO to SiO₂ were investigated as functions of gas mixing ratio, rf power, dc-bias voltage, pressure and gas flow. To understand the effects of etching parameters, the atoms of B, Cl and the ions of Ar were investigated in BCl₃/Ar plasma using optical emission spectroscopy and Langmuir probe. The etching byproducts were investigated with using quadruple mass spectroscopy. The heterogeneous reaction of plasma on the surface of the etched LNO was investigated with x-ray photoelectron spectroscopy and secondary ion mass spectroscopy. The etching profiles of samples have been investigated with scanning electron microscopy.

PS-TuP7 Plasma Etching of Cantilever Epitaxy Sapphire Substrates, K.C. Cross, K.H.A. Bogart, C.C. Mitchell, R.D. Briggs, Sandia National Laboratories
Growth of GaN-based wide bandgap semiconductors by MOCVD is performed on sapphire, silicon carbide, or silicon substrates due to the lack of bulk crystalline GaN. Cantilever epitaxy (CE), a new lateral overgrowth method, utilizes sapphire substrates patterned by plasma etching. CE is advantageous because it requires only one growth run to achieve <E7 dislocations per cm², nearly one to two orders of magnitude lower than standard planar growth. The sapphire (Al₂O₃) material is exceedingly difficult to etch due to the large Al-O bond strength (122.4 kcal/mol). We have developed a method for plasma etching of sapphire. The etching mask for the sapphire is a quad-level film stack consisting of a release layer, hardbaked photoresist, silicon nitride, and imaging resist, and is etched in an ECR plasma with O₂/Ar chemistry. The sapphire is etched in an ICP system with high rf source and substrate powers, low pressure and temperature, and chlorine-based chemistry. Typical etching rates are 580 Å/min with a selectivity of 0.3, for etch depths of 2-4 μm. Issues that have been difficult to overcome include etch uniformity over 50 mm, critical dimension control, and profile control. Data and optimization of the etching process will be presented. Results from experiments to characterize the etching process as a function of rf source power, substrate bias, pressure, temperature, and gas chemistry will also be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

PS-TuP8 Effect of O₂/Cl₂ Gas Mixing Ratio on Dry Etching Characteristics and Electrical Properties of Bi_{4-x}La_xTi₃O₁₂ Films, D.P. Kim, C.I. Kim, K.T. Kim, Chung-Ang University, Korea; A.M. Efremov, Ivanovo State University of Chemistry and Technology, Russia

Recently, Bi_{4-x}La_xTi₃O₁₂ (BLT) has been considered a predominant candidates for ferroelectric random access memory because of its high resistance to polarization fatigue due to Bi₂O₂ layers, which reduce space charges and the unpinning of domain walls. There are a lot of reports on deposition BLT thin films, but there is no report on the etching characteristics and electrical properties of BLT in Cl₂/O₂ plasma. The BLT of 200 nm was spun-coated on a Pt/Ti/SiO₂/Si substrate by MOD. Pt thin films, which used as top electrode, were deposited on BLT. BLT thin films were etched in Cl₂/O₂ using ICP because it is easy to control energy of infringing ions to the substrate. When Cl₂-based gas mixtures were used with Ar and O₂, the etch products remaining on the substrate could be observed after etching because of their very low vapor pressure. The etch rates and selectivity of BLT thin films were investigated as a function of gas mixing ratio, rf power, dc-bias voltage, and pressure. With adding 20% O₂ in Cl₂ plasma, increasing rf power and dc bias voltage and lowering pressure, the etch rate of BLT increased. To understand the effects of etching parameters on the etch rates of BLT thin films, the atoms of Cl and O investigated using

optical emission spectroscopy and Langmuir probe. The surface of the etched BLT was investigated with x-ray photoelectron spectroscopy. To estimate electrical properties of BLT after etching process, the etched species were characterized with measuring leakage current using semiconductor parameter analyzer [HP4145B] and P-E loops of Pt/BLT/Pt capacitor using precision work station. In Cl₂/O₂ plasma, we obtained higher low remnant polarization value and lower leakage current density compared with Cl₂/Ar plasma. @FootnoteText@
Acknowledgement: This work was supported by grant No. R01-2001-00268 from the Korea Science & Engineering Foundation.

PS-TuP10 Production of Electron-Temperature-Controllable ECR Plasma for Thin Film Deposition, N. Itagaki, H. Muta, Kyushu University, Japan; N. Ishii, Tokyo Electron Co. Ltd., Japan; Y. Kawai, Kyushu University, Japan
In semiconductor processing, it is required to control the electron temperature (T_e) in the plasma for progress of microelectronic devices and minimization of substrate damage. An electron cyclotron resonance (ECR) plasma source has attracted much attention for its high electron density that can be achieved at low gas pressure. However, in a conventional ECR plasma produced by 2.45 GHz microwave, T_e is relatively high and quite hard to be controlled in a wide range. Recently, we have clarified that T_e in a 915 MHz ECR plasma depends on the spatial profiles of the microwave power absorption by both the measurement of electromagnetic waves and the calculation of microwave power absorptions. Since the power absorption profile is influenced by the effective resonance zone width (Δz_{res}, above-mentioned results implies that T_e can be controlled by varying Δz_{res} which is determined from the magnetic field gradient and the microwave frequency. In this report, the spatial profiles of wave patterns were measured at different Δz_{res} to make clear the relationship between the power absorption profiles and Δz_{res}. Furthermore, we tried to control T_e by changing the magnetic field gradient in order to examine whether or not the above-mentioned way to control T_e is an effective method. As a result, the power absorption profiles were confirmed to change with Δz_{res}, which indicated that T_e could be controlled by varying Δz_{res}. In fact, we observed that T_e varied from 1.9 eV up to 3.5 eV with increasing the magnetic field gradient at the resonance point from 0.3 G/mm to 1.4 G/mm for N₂ plasma. The experiments on thin film deposition were also performed to investigate the relationship between T_e in the plasma and the quality of prepared films, which will be presented at the conference.

PS-TuP11 Fabrication of Carbon Nanowalls Using RF Plasma-Enhanced Chemical Vapor Deposition Assisted by Hydrogen Radical Injection@footnote 1@, K. Shiji, M. Hiramatsu, T. Kadoya, H. Amano, Y. Ando, Meiji University, Japan; M. Hori, Nagoya University, Japan
Carbon nanostructures are of tremendous interest from both a fundamental and an applied prospective. Recently, fabrication of two-dimensional carbon nanostructures (carbon nanowalls) was reported.@footnote 2@ The large surface area of carbon nanowalls may provide us various new applications. In the case of film formation using plasma-enhanced chemical vapor deposition (PECVD) technique, surface morphology can be effectively controlled not only by optimizing the substrate temperature and bias, but also by the inclusion of specific reactive species as appropriate to the film growth and nucleation. Previously we demonstrated the diamond growth using a unique PECVD system that consists of a parallel-plate radio-frequency (rf, 13.56 MHz) capacitively coupled plasma (CCP) assisted by a hydrogen (H) radical source.@footnote 3@ In this work, carbon nanowalls were successfully fabricated on silicon (Si) substrate using C₂F₆/rf-CCP assisted by H radical injection from H₂ inductively coupled plasma (ICP). Partial pressures of C₂F₆ and H₂ were 20 and 80 mTorr, respectively, and the total pressure was 100 mTorr. The rf powers of CCP and ICP were 100 and 400 W, respectively, and the substrate temperature was 500 °C. Growth experiments were conducted for 2 hours. Carbon nanowalls were grown vertically on the Si substrate without catalyst. The thickness of these carbon nanowalls grown was 10-30 nm, and their height was about 300 nm. The aggregation of carbon nanowalls would be useful as templates for the fabrication of other types of nanostructured materials. In the case of the deposition without ICP, on the other hand, carbon nanowalls were not fabricated. @FootnoteText@
@footnote 1@This work was supported by 21st century COE program, Nano Factory.@footnote 2@Y.H. Wu, et al., Adv. Mater., 14 (2002) 64. @footnote 3@M. Hiramatsu, et al., Rev. Sci. Instrum., 67 (1996) 2360.

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PS-TuP12 Surface and Gas-phase Reactions in Plasma CVD using Cu(EDMDD) as Source Material, K. Takenaka, M. Takeshita, M. Kita, K. Koga, M. Shiratani, Y. Watanabe, Kyushu University, Japan; T. Shingen, Asahi Denka Kogyo K.K., Japan

We have demonstrated 1) deposition of Cu films which have a low resistivity of $1.85 \mu\Omega/\text{cm}$ and a strong adhesion strength above 10 MPa to the TiN layer, and 2) conformal deposition of smooth Cu films of 20 nm in thickness in trenches $0.5 \mu\text{m}$ wide and $2.73 \mu\text{m}$ deep using H-assisted plasma CVD (HAPCVD), which has an advantage of controlling independently concentrations of Cu-containing radicals and H atoms. To obtain information on surface and gas-phase reactions in HAPCVD, we have studied electron impact dissociation processes of Cu(EDMDD) as well as nucleation and island growth of Cu, which are closely related with smoothness of Cu films and their adhesion strength to their under-layer. Quadrupole mass spectroscopic measurements show that Cu^+ is the dominant ionic product from Cu(EDMDD) due to an electron impact at electron energy of 70 eV. Based on this result together with the ion-core model, Cu(EDMDD) is suggested to be the main neutral radical from Cu(EDMDD) due to electron impact dissociation. In-situ FT-IR measurements also show that supply of H atoms to the surface of deposition film is quite effective in reducing its impurity concentration. Nucleation density has little dependence on the kind of materials of under-layer such as TiN, TaN, WN, and Si. The nucleation rate increases from $2.3 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}$ at the substrate temperature $T_s = 120^\circ\text{C}$ to $4.1 \times 10^{14} \text{ m}^{-2} \text{ s}^{-1}$ at $T_s = 220^\circ\text{C}$ with increasing T_s , while a maximum nucleation density of $3 \times 10^{16} \text{ m}^{-2}$ is obtained at $T_s = 150^\circ\text{C}$. The maximum density is more than two orders of magnitude higher than that for thermal CVD, and the high density is considered to contribute to smoothness and high adhesion strength of Cu films. K. Takenaka, et al., Proc. of ISTC 2002 (in press).

PS-TuP13 Sub-Millimeter Absorption Measurements of Temperature and Density in Fluorocarbon Plasmas, E.C. Benck, K. Siegrist, D. Pusquell, National Institute of Standards and Technology

Sub-millimeter (300 GHz to 1 THz) absorption spectroscopy is being developed as a diagnostic for measuring radical densities and temperatures in processing plasmas for microelectronics. Most molecules, radicals, and ions have transitions suitable for detection at these frequencies and the necessary spectroscopic data is available in the literature for determining the absolute radical densities. Initial measurements are being conducted with a backward-wave-oscillator (BWO) source and a liquid-He-cooled bolometer detector. The narrow linewidth ($< 10 \text{ kHz}$) of the BWO is ideally suited for measuring the translational temperatures of radicals through the Doppler broadening of the absorption lineshape. Previous temperature measurements in an inductively coupled Gaseous Electronics Conference (GEC) Reference Reactor found all the radicals to have a translational temperature close to room temperature. Other spatially resolved plasma diagnostics, such as laser-induced fluorescence, in similar inductive sources found significantly higher rotational temperatures within the plasma. The disagreement between the diagnostic methods is being investigated by measuring the radial density and temperature distributions. Initial results indicate that the low temperatures being measured with the BWO are probably due to the geometry of the GEC Reference cell which has a large volume of gas surrounding the plasma. Therefore the line-integrated absorption signal of the BWO is being dominated by the cooler, denser gas surrounding the plasma.

PS-TuP14 Plasma Frequency Measurements for Absolute Plasma Density by Means of Wave Cutoff Method, J.H. Kim, Korea Research Institute of Standards and Science, Korea; Y.H. Shin, K.H. Chung, Korea Research Institute of Standards and Science

A plasma oscillation method and a plasma absorption method have been used for measurements of absolute electron density in a plasma. In this report, a newly designed method for precise measurements of absolute electron density in the plasma using plasma frequency is described. A microwave perturbation of a frequency is introduced to plasma from a network analyzer and transmits in the plasma. The transmitted wave at a distance from a radiating antenna is monitored using spectrum analyzer as scanning the perturbing frequency. The transmitted wave rapidly decays by wave cutoff at the plasma frequency, which gives the absolute electron density. The propagating waves of some frequency including plasma frequency are characterized. The measured plasma frequency by this method is coincident with that obtained by the

plasma oscillation method. The measured plasma densities are also compared with those got by using a double Langmuir probe over wide parameter range (gas composition, input power and gas pressure). T. Shirakawa and H. Sugai, Jpn. J. Appl. Phys. Vol. 32, 5129 (1993). H. Kokura et al., J. Appl. Phys. Vol. 38, 5262 (1999). K. Nakamura et al., J. Vac. Sci. Technol. A 21, 325 (2003).

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