Tuesday Afternoon Poster Sessions

Plasma Science and Technology

Room: 4C - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Selective Etching of SiO_2 over Si_3N_4 in Triple Frequency Capacitively Coupled Plasma System, ***H.-G. Lee***, *S.-O. Lee, M.-S. Lee, S.-H. Cho, S.-K. Lee, S.-C. Moon, J.-W. Kim*, HYNIX Semiconductor Inc., Republic of Korea

It has been reported that the triple frequency (60MHz, 27MHz, 2MHz) capacitively coupled plasma (CCP) system provides more advanced process performance and wider process window for etching dielectric films compared to conventional dual frequncy (60MHz, 2MHz) CCP system. In this study, the effect of triple frequency with the bottom electrode in $C_4F_6/O_2/Ar$ gas plasma on the selective etching of SiO_2 over Si_3N_4 is considered as a function of the power applied to each frequencies. To understand the characteristics of triple frequncy concerning etch selectivity of SiO_2 over Si_3N_4, we considered the chemical species such as CF_2 radicals and other radicals that have influence on polymerization using optical emission spectroscopy (OES). The thickness of deposited polymers and components in this triple frequency CCP system were investigated by high resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS).

PS-TuP2 Etching Characteristics of V_2O_5 Thin Films using by Cl_2/Ar Inductively Coupled Plasma, ***C.M. Kang***, *C.I. Kim*, Chungang University, Korea

Recently, the technology of microelectronic systems has attracted global attention for applications such as medical devices, communication systems, sensors and actuators. Vanadium oxide has a high capacity for ion storage, it is stable under a cyclic voltage and provides a particular (mixed) type of coloration complementary to that exhibited by the tungsten oxide (WO_3), allowing the production of high performances smart windows. Also vanadium oxides, with unique characteristic structures, comprise a particularly interesting group of inorganic 3d-transition metal oxide compounds due to their diverse, electronic, opto-electronic, electrochromic, and magnetic properties, which makes them potential candidates for important technological applications. Research and development of V_2O_5 have been rapidly accelerated to improve materials for the last decades. But, etch properties of V_2O_5 have not established yet. In this study, we investigated etch characteristics of dry etching of the V_2O_5 thin films in the inductively coupled plasma etch system with (Cl_2/Ar) gas mixture. The etching characteristics of V_2O_5 thin films were investigated in terms of etch rates and selectivity as a function of (Cl_2/Ar) gas mixing ratio, rf power, dc bias voltage and chamber pressure. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) was used to investigate the etching profile.

PS-TuP3 Advanced Gate Stack Processes for sub-70nm CMOS Technology, ***G.H. Kim***, *K.T. Kim, C.I. Kim*, Chung-Ang University, Korea

The continued evolution of MOS (metal-oxide-semiconductor) transistor beyond the 90nm technology node will most likely be driven by advances in materials engineering and process integration. Fundamental changes in the materials used in the MOSFET (MOS field effect transistor) gate stack will become necessary as will novel processing techniques. High-k dielectrics can potentially extend scaling to thinner equivalent oxide thickness. However, in the production of very small size devices, the fine patterning technology is very important in order to manufacture the detailed device design based on the principle of the device operation. In this work, the dry etchings of new materials studied for the future CMOS devices are described. TiN as the metal gate electrode material and high-k gate insulators such as HfO_2 and Al_2O_3 are investigated. Etch rates and etch selectivity of TiN/high-k dielectrics gate-stack structures on Si substrate were investigated by varying the process parameters such as gas mixing ratio, source RF power, DC bias voltage, and process pressure. Plasma diagnostics were performed by quadrupole mass spectrometer (QMS) measurements and optical emission spectroscopy analysis. To investigate the etch residues of the high-K dielectric is generated by $BCl_3/Cl_2/O_2$ plasmas, the surface analysis on the dielectrics was performed using x-ray photoelectron spectroscopy (XPS).

PS-TuP4 Etching Characteristics of High-k Dielectric Materials in Inductively Coupled $Ar/CF_4/C_4F_8$ Plasma, ***S.W. Kim***, *B.J. Park*, Sungkyunkwan University, Korea, *S.-K. Kang*, SKKU Advanced Institute of Nano Technology, Korea, *K.S. Min, S.D. Park, G.Y. Yeom*, Sungkyunkwan University, Korea

For the next generation metal oxide semiconductor field effect transistor (MOSFET), high-k materials such as HfO_2, ZrO_2, BST, etc. are required as gate dielectric materials which replace SiO_2/Si_3N_4. To apply these high-k materials to the next generation devices, the etch characteristics needs to be satisfied in addition to the adequate materials characteristics. For these materials, precise etch rate is required instead of high etch rate due to the low thickness of the material and extremely high etch selectivity over underlayer material is required. Also, no damage or residue remaining on the etched surface is tolerable. In this study, the etch characteristics of high-k materials such as HfO_2 and ZrO_2 were investigated as a function of gas mixture composed of $Ar/CF_4/C_4F_8$ using an inductively coupled plasma etcher, and the effect of gas mixture on the etch rate, etch selectivity to silicon, the remaining C-F polymer on the silicon surface, and the damage to the MOSFET device were investigated. In the presentation, the change of materials physical, chemical, and electrical properties etched by $Ar/CF_4/C_4F_8$ using an inductively coupled plasma etcher will be shown in details with the properties of MOSFET devices fabricated by $Ar/CF_4/C_4F_8$ ICP.

PS-TuP5 The Etching Mechanism of Zinc Oxide Thin Films for Optoelectronics Device Application using Inductively Coupled Plasma, ***J.C. Woo***, *K.T. Kim, G.H. Kim, C.I. Kim*, Chung-Ang University, Korea

Zinc oxide (ZnO) exhibits an interesting combination of multifunctional properties, including optical, piezoelectric, and optoelectronic properties, and in thin film form ZnO films find immense applications in many electronic devices including sensors, transducers, and high frequency surface acoustic wave (SAW) devices. It has advantage relative to GaN because of its availability in bulk, single-crystal form, and wide bandgap energy of 3.4 eV, which makes it transparent to visible light. The excition binding energy is ~60 mV for ZnO, as compared to GaN, ~25meV; the higher excition binding energy enhances the luminescence efficiency of light emission. Research and development of ZnO have been rapidly accelerated to improve materials for the last decades. But, etch properties of ZnO have not established yet. Accordingly for many application optoelectronic devices, the etching mechanism of ZnO thin films during the etching process must be understood. However, few of etching mechanism was examined in our previous works and it can be hardly etched. So it is very important to improve the high etch rate, vertical etch profile, smooth etch surface, high mask selectivity and smooth sidewalls for developing ZnO thin films. In this study, we investigated etch characteristics of the ZnO thin films in the inductively coupled plasma system. The etching characteristics of ZnO thin films were investigated in terms of etch rates and selectivity as a function of additive gas mixing ratio. The plasmas were characterized by optical emission spectroscopy analysis and quadrupole mass spectrometer measurements. The chemical reaction on the surface of the etched ZnO thin film was investigated with X-ray photoelectron spectroscopy. Scanning electron microscopy was used to investigate the etching profile.

PS-TuP6 Study of the Amorphous Silicon Etching using Pin to Plate Dielectric Barrier Discharge in Atmospheric Pressure Plasma, ***S.J. Kyung***, *J.B. Park, J.H. Lee, G.Y. Yeom*, Sungkyunkwan University, Korea

In this study, atmospheric pressure plasmas were generated with a modified dielectric barrier discharge (pin-to-plate DBD) having the power electrode composed of multi-pins instead of a conventional blank planar plate and their characteristics of discharge were investigated. The effect of CF_4 in the N_2/NF_3 gas mixture on the characteristics of the pin to plate dielectric barrier discharge (DBD) having the size of 170 x 100 mm have been investigated for the application to thin film transistor liquid crystal display (TFT-LCD) processing such as amorphous silicon(a:Si) and silicon nitride(Si_3N_4) etching. The result showed that the selectivity of a:Si/ Si_3N_4) was increased with CF_4 flow rate in N_2/ NF_3 up to 250 sccm, however, the further increase of CF_4 flow rate decreased the selectivity of a:Si/ Si_3N_4). A maximum etch rate of a:Si of 110 nm/sec with the selectivity of a:Si/ Si_3N_4) of 5.1 could be obtained with a gas mixture of 250 sccm CF_4 in N_2 (50 slm)/ NF_3 (300 sccm) and at 8.5 kV of AC rms voltage.

PS-TuP7 Effect of Gate Processing on Line edge Roughness in 45nm, *P.K. Subramanian, **I. Matthew**, T. Wallow,* Advanced Micro Devices*, L. Tsou*, IBM Corporation

As gate lengths shrink in 45nm technology node and beyond, the variation contributed by Line Edge Roughness(LER) becomes a larger proportion of the total CD variation Therefore, a reduction in the LER is one way of reducing the total variability of gate dimensions across a chip. In this paper we study evolution of the LER through the various process steps that end with the formation of a gate on the wafer. We examine the frequency components of the roughness as the wafer processed through various (lithography and etch) steps and examine the effects of each of these processes on the roughness spectrum. The advent of the immersion lithography and the attendant higher Numerical Aperture(NA) has led to the adoption of new schemes to reduce reflectivity. The impact of the new lithographic schemes on LER evolution is also examined. We also examine the effects of modifying etch process parameters and chemistry on the roughness spectrum. The effect of HBr plasma curing during etch processing on the LER is studied.

PS-TuP8 Directional Oxidation of Silicon Trench in Surface Wave Oxygen Negative Ion Plasma, *H. Shindo, T. Mitomi, M. Suzuki, **K. Kusaba***, Tokai University, Japan

A low temperature and low damage silicon oxidation technique is highly required in various ULSI processes. In particular for trench isolation of a memory cell to realize further integrations, the oxidation should be ion-assisted for directionality but with low damage. Additionally, a new type of MOS transistor with a trench gate has recently been proposed for the next generation of ULSI. For this purpose, a new method of negative ion assisted silicon oxidation has been proposed employing microwave oxygen plasmas. In this work, a new method of negative ion assisted silicon oxidation is proposed employing microwave oxygen plasma, and a directional and low temperature silicon trench oxidation will be demonstrated. The oxidation characteristics were intensively studied in silicon trench to form a shallow trench insulation layer for cell isolation of MOS transistor. The plasma was produced in an aluminum chamber 240 mm in diameter. At the one end of the chamber, a microwave of 2.45 GHz was introduced through a high permittivity material of AlN (permittivity: 10.9) window of disc plate. The oxidation characteristics were precisely examined in a silicon trench of 0.15 um width and 0.2 um depths. The oxidation was made in the condition of 400 degree C and the bias frequency of 1900 kHz. The oxidation depth at the three positions of the trench was determined from SEM photograph. These three positions are labeled as “Top, Side and Bottom” The oxidation depth at all positions was at first decreased with an increase in the axial distance from the microwave window, but it was increased again in the downstream. Particularly, the oxidation depth at the trench bottom showed a maximum in a very downstream of 18 cm from the window, and thus the step coverage of the trench oxidation, defined as the depth ratio of the trench bottom to the top, reached as high as 0.8. Since the axial distance at which the oxidation depth begins to increase again is just coincident with the region where the electron energy is rapidly decreased, this directional oxidation feature is ascribable to the negative oxygen ions. It is concluded that the oxidation by high density oxygen surface-wave plasma with high permittivity window is innovative.

PS-TuP9 Dry Etching Technology of Cobalt Silicide for sub-60nm Gate Patterning using ICP Source with High Temperature ESC, ***H. Lee***, Samsung Electronics, Korea*, J.I. Shin, H.S. Lee,* Applied Materials*, D.H. Kim*, Samsung Electronics, Korea*, T.W. Kim,* Applied Materials*, K. Shin, M.C. Kim, G.J. Min, C.J. Kang, J.T. Moon*, Samsung Electronics, Korea

Dry etching of $CoSi_2$ gate in sub-60nm design rule is successfully done using ICP (Inductively Coupled Plasma) source with high temperature ESC (Electro-Static Chuck). Vertical profile is achieved by forming a volatile Co byproduct reacted with Cl_2/Ar based plasma at 250°C of ESC temperature under relatively low DC bias voltage (~300V). Since Cl_2/Ar based plasma has low etch selectivity to polycrystalline Si (poly-Si) and gate oxide, O_2 and N_2 were added to reduce the recess of poly-Si layer which is remained beneath $CoSi_2$ layer during silicidation process. $CoSi_2$ layer used in this experiment was formed by sintering of sputtered Co layer on poly-Si layer. Dry etching of poly-Si is followed with both low temperature(~80°C) and high temperature (~250°C) ESC after $CoSi_2$ etching. For the poly-Si etching, HBr/O_2/He plasma was used to maintain high selectivity to gate oxide. However, even though poly-Si layer is recessed more than 200Å during $CoSi_2$ etching process, it was not possible to remove remaining poly-Si completely with HBr/O_2/He plasma. TEM and EDX are used to analyze surface of poly-Si, and thin metal layer containing Co is observed on the surface of polycrystalline Si layer. It is believed that this thin metal layer blocks etching of poly-Si. Therefore, removing the thin metal layer or preventing re-deposition of Co byproduct on polycrystalline Si layer during $CoSi_2$ etching will be necessary. Co as a barrier metal of bit line is also etched with vertical profile on high temperature (~300°C) ESC with Cl_2/Ar plasma. In this case, there was no remaining Co by-product since enough amount of Co OE is possible, resulting in complete removing of Co byproduct on ILD.

PS-TuP10 Stripe and Hole Shape Contacts Etch for Power Amplifier BICMOS Devices, ***J.P. Oddou***, *D. Ristoiu, J. Mourier*, STMicroelectronics, France

Power amplifier applications of BICMOS devices need a specific contact module in order to support high current density and temperature. In order to achieve such performances, stripe-shaped contacts are designed for the bipolar transistor, while classic hole contacts are used for CMOS and the contact depth is increased to 1.5µm. Therefore, taking into account the topography of the bipolar and MOS structures, 5 different types of contacts must be opened. To fulfill these specifications, contacts etch process requires: - sharp profile to achieve high depth contacts; - high selectivity of oxide to nitride to safely land on emitter, gate and active areas; - low loading effects to achieve both stripe and hole contacts having the same critical dimension (CD). In this paper we focus on oxide etch process for contact opening developed on a MERIE industrial etcher using C5F8/ O2/ Ar chemistries. In a first time we characterize the oxide to nitride selectivity and the profile slope as a function of the C5F8/O2 ratio. Higher C5F8/O2 ratio favors selectivity, but degrades slope and CD, while lower C5F8/O2 ratio leads to sharp profile in the detriment of selectivity, therefore our approach consists in using a sequence of etching steps having different C5F8/O2 ratio. We demonstrate that this process solution enables us to achieve the above mentioned morphological constraints. Moreover, electrical tests performed on contact chains show that the resistivity and leakage results are in line with technology specifications.

PS-TuP11 Sidewall Passivation Effect during C_4F_8 + N_2 Etch Process for SiOCH Low-k Films, ***S.-K. Yang***, *H.-S. Yoo,* Inha University, Korea*, H.-Y. Song,* Samsung Electro-Mechanics Co. LTD., Korea*, J.-G. Lee,* Bucheon College, Korea*, S.-G. Lee, B.-H. O, I.-H. Lee, S.-G. Park*, Inha University, Korea

Plasma induced damage to low k dielectric layer is one of key issues in developing the multi-level interconnection technology based on Copper and low k dielectrics. Change in chemical bonds and contents of carbon or fluoride often results in higher dielectric constant. In this work, etching of SiOCH low k films was studied by C_4F_8 + N_2 plasma in Inductively coupled plasma etcher. X-ray photoelectron spectroscopy showed C-F and C-N bondings on the sidewall of patterned low k dielectric layer, which indicated the formation of passivation film. This passivation layer remained after photoresist removal by N_2 plasma and even after dipping in 1% HF solution. It is shown that patterning of SiOCH layer by C_4F_8 + N_2 plasma caused the increase in dielectric constant k by forming C-F passivation films.

PS-TuP12 Critical Dimension Shrink and Control with Different Frequency Source Powers in Dielectric Etch Chamber for 45nm Technology and Beyond, ***J. Wang***, Applied Materials

The Critical Dimension (CD) shrink from BARC was invested by using the capacitive coupled plasma etcher with high frequency source due to BARC open step is the most critical in dielectric etch. Two frequencies (<100MHz vs >100 MHz) source power with different plasma densities were compared. It was found that the CD shrink was related to the CF2 species that were excited from source and>100 MHz source power showed the strong control knob on CD shrink comparing to <100MHz. Chemistry selection and process control knobs have been evaluated and it was found that the CD shrink was basically controlled by pressure, polymer gas, and source power. And a maximum >60nm CD shrink bias was obtained when profile and final CD range was maintained in the spec. (1) CD bias comparison on the BARC open with and without source power indicated source power strong effect on CD shrink. The CF2 radical emission in etching plasma were collected by the optical emission spectroscopy (OES) as shown to evaluate the difference on the CD shrink when other process parameters changed . It was found that the >100 MHz source provided the efficient generation of CF2 radical density that resulted in more CD shrink. The CD shrink varied with different source power for both frequencies and it showed the more CD shrinks with high source power. The CF2 species density without source power showed lowest signal and the strongest emission with the high source power, which was pretty much consistent with the wafer results. (2) CHF3 flow on BARC open was tested at different pressure and the high CHF3 gas flow and low pressure were showing strong knobs on CD shrink control with source power. It was known that CF2 was one of many species from CHF3 dissociation during the plasma etch and more CF2 has been generated with high frequency power, which deposited on the sidewall to protect the isotropic etch and therefore made the top CD shrink. With the low CHF3, the CD shrink range was much bigger than high CHF3 flow with pressure change. The CF2 species density explained why

high source power and low pressure as the knobs on CD shrink control. (3) The production-like runs on customerâ?Ts wafers were tested with two source powers and both showed CD shrink consistently repeatable. The high frequency source power provided the high plasma density as the strong knob for CD shrink and meantime allowed the high efficiency wafer-less dry clean, which benefited APF etch clean mode requirement.

PS-TuP13 Analysis of High Aspect Ratio Contact Etch using High Flow Concept, ***S.-J. Park***, *S.-C. Park, Y.-J. Kim, W.-S. Han*, Samsung Electronics Co. Ltd., Korea

As contact sizes scale down below 100nm, high aspect ratio contacts (HARC) encounter the limits such as the low selectivity of the resist material, etch stopping mechanism, the profile distortion, and so on. The high flow concept is a widely used scheme for RIE (reactive ion etching) technology. The rapid movement of reactive ion sources affect on the dissociation mechanism of the etching chemistry. The carbofluoride (CxFy) chemical sources show different behaviors, while the flow rate changes at the same pressure. The QMS (quadrapole mass spectroscopy) method enables the analysis of the dissociated chemicals and the byproducts during HARC etch. The ratio of carbofluoride and fluorine seem to be the major factor which determines the profile of HARCs and the resist selectivity. The contact patterns with an aspect ratio of 30 are used to identify the high flow concept in this experiment. The flow rate of carbofluoride chemistry changed up to 2.8 times higher than the normal reference flow rate in a CCP (capatively coupled plasma) chamber. The higher flow rate improves in terms of the resist selectivity. However, the profile distortion between the top opening and the bottom opening is worse than the profiles under the normal condition. The HARC etch study at the high flow condition will be shown in terms of the profile distortion and the real time chemistry monitoring using QMS method.

Keywords : RIE, HARC, high flow.

PS-TuP14 Improvement of Sputter Deposited Mo-based Barrier Films by Insertion of a Thin Al Interlayer for Copper Metallization, ***P. Majumder***, *C.G. Takoudis*, University of Illinois at Chicago

Copper is used as interconnects in advanced ultra large scale integration microelectronic devices due to its low electrical resistivity and superior resistance to electromigration compare to Al. However, Cu diffuses easily into Si and SiO_2, and forms copper silicide compounds at temperatures as low as 200 °C, resulting in degradation of Si devices at low temperature. Therefore, the use of diffusion barriers between Cu and Si becomes essential in order to successfully implement copper as an interconnecting metal. Sputter-deposited refractory metals, like W, Ta, Mo, and Ti and their nitrides have been recognized as diffusion barriers due to their high thermal stability, low resistivity and excellent capability of suppressing reactions between Cu and Si. In recent years, Mo-based diffusion barriers have been investigated for copper metallization. Many studies show that sputtered deposited Mo and MoN_x barrier layers are polycrystalline in nature and thus failed after annealing at relatively lower temperatures due to the diffusion of copper through the grain boundaries of the polycrystalline films. In this work, we investigate the barrier performance of sputtered deposited Mo and MoN_x due to the insertion of ultrathin Al interlayer. Al is used to stuff the grain boundaries of Mo and MoN_x thereby increasing the breakdown temperature of the barrier films. Mo and MoN_x films are sputtered deposited using Ar and Ar/N_2 mixture, respectively, under a 4.5 mtorr total sputtering pressure. The formation of crystallites takes place on the surface of the copper layer at the barrier failure temperature. The quantitative analysis of these crystallites is done using energy-dispersive spectroscopy. The thermal stability of Mo-based barrier layers are evaluated after annealing at wide range of temperatures in the presence of N_2 using four probe measurements for sheet resistance, X-ray diffraction analysis for phase identification and scanning electron microscopy for surface morphology. The interaction of different layers due to high temperature annealing is evaluated by depth profiling using X-ray photoelectron spectroscopy.

PS-TuP15 Ar Ion and Ammonia Modification of OSG Surfaces: A Novel Route to Nanoscale Diffusion Barriers, *J. Wilks*, ***J.A. Kelber***, University of North Texas

The continued scaling of barriers to < 4 nm thickness drives the quest for a practical single step deposition process, in contrast to the current TaN/Ta two step standard. Pure Ta deposition has been considered, but Ta deposition on OSG and related materials results in a Ta-O-C "interphase" 2-4 nm thick which inhibits Cu adhesion and prevents barrier scaling to sub-4 nm length scales. We present in-situ XPS and ex-situ AFM data indicating that 500 eV Ar ion bombardment in the presence of ammonia results in a self-limiting process involving carbon depletion and nitrogen addition to the surface region. No significant change in surface rougness is observed. The surface nitridation results in a qualitatively different response to Ta deposition: an abrupt interface with initial Ta2N formation, with subsequent Ta formation at longer deposition times. These results suggest a new direction in plasma pretreatment of OSG surfaces prior to metallization--a self-limiting surface nitridation, followed by a single step Ta PVD process resulting in a Ta2N/Ta nanoscale barrier. Further, the results observed for the ion bombardment process mimic in major respects results observed for low pressure plasma treatments--including enhanced carbon depletion due to the presence of ammonia, the self-limiting nature of the process, and nitrogen incorporation. The usefulness of such UHV-based processes as models for low-pressure plasma processing will also be discussed.

PS-TuP16 Size Distribution Factor of Platinum Nanoparticles Synthesized by Plasma in Aqueous Solution, ***T. Nishigaki***, *T. Ishizaki, N. Saito, O. Takai*, Nagoya University, Japan

Well-defined platinum nanoparticles activate of photo catalysis, decompose harmful component in exhaust gas of automobile, lead to high potential of fuel cell. Platinum nanoparticles have been synthesized by various techniques including chemical reduction, photo reduction and electrochemical technique. However, in these techniques, it takes few hours to synthesize the nanoparticles or chemically toxic substances leave in a product. Now, it is required to develop a green process rapidly to synthesize nanoparticles. We have developed 'Solution Plasma', which is defined as plasma in aqueous solution. Solution plasma has attracted much attention as a novel chemical reaction field. As solution plasma generates UV light, electrons, and radicals, higher reaction rate would be achieved. In this study, we aimed to synthesize platinum nanoparticles by solution plasma. In addition, we investigated influence of solution pH on the sizes of the platinum nanoparticles. Optical absorption of nanocolloidal platinum was measured by UV-vis spectrometer. The nanoparticles were observed by transmission electron microscopy (TEM). $H_2PtCl_6?6H_2O$ (1.44mM) and PVP (Polyvinylpyrrolidone, 12.1mM) were used as row materials. The pH of solution was varied from 2.5 to 4.5. The electrical conductivity was adjusted to 1.5mS/cm by the addition of KCl. A pulsed power supply was utilized to generate plasma. Pulsed voltage of 1.6kV was applied between the tungsten electrodes in the solution. Pulse width and frequency were varied from 2.0 to 3.0μs, respectively. Solution color changed from orange to dark brown at discharge times of more than 40 min. An absorption peak at 262 nm originated from $PtCl_6^{2-}$ became weaker with the increases of the discharge time, while baselines in the spectra became higher in all the range. These results indicate the formation of platinum particles. TEM image shows that the mean diameter of the nanoparticles was 10nm. Debye rings by (111), (200), (220), (311) were also observed by diffraction patterns. The effects of pulse width, frequency and pH on the particle size distribution were also discussed.

PS-TuP17 Effects of Ions and Radicals on the Growth of Single-Walled Carbon Nanotubes Produced by Diffusion-Plasma CVD, ***T. Kato***, *R. Hatakeyama*, Tohoku University, Japan

Individual single-walled carbon nanotubes (SWNTs) have attracted a great deal of attentions since the discoveries of their prominent electrical and optical characteristics. Recent progresses in a synthesis stage of the isolated SWNTs provide outstanding opportunities to efficiently study the basic science of ideal one-dimensional materials. A plasma CVD is well-known as a nanotube formation method including outstanding benefits in the vertical growth of individual multi-walled carbon nanotubes. Up to now, our group firstly demonstrated that those benefits in the plasma CVD can be also applied to the SWNT growth stage, and the freestanding individual SWNT growth on a flat substrate has been achieved with a diffusion plasma CVD method. These progresses of a plasma technology in the nanotube fabrication field can strongly accelerate industrial application of SWNTs. Unfortunately, however, any quantitative discussion about effects of plasmas on the growth of SWNT has not been realized at all so far, and it is one of inevitable issues to fully utilize potential abilities of plasmas for a realistic use of SWNT-device applications. These backgrounds motivate us to investigate the detailed effects of plasmas on the growth of SWNTs. In our study, the effects of ion energy and radicals are mainly focused with a precisely parameter- controlled diffusion plasma CVD system. Derived from the carefully investigated experimental results about the time evolution of SWNT growth, the simple equation is established to describe the growth kinetics of SWNTs during the plasma CVD. Based on the fitting of the experimental result with the equation, remarkable effects of ions and radicals are uncovered. There are clear threshold energies of ions for the destruction of the tube structure. It is conjectured that those threshold energies correspond to that of the bond breaking between carbon in the nanotube and the displacement of the carbon atom from a graphite network in the nanotube. In the case of the radicals, the etching rate during the SWNT growth is found to be strongly influenced by the amount of atomic hydrogen in the plasma. Furthermore, a unique correlation is also identified between the incubation time of the SWNT growth and density of ions in the plasma. These discoveries of the interesting correlations between the

detailed growth parameters of SWNTs and key elements in plasmas could contribute to the further advance for the perfect structure control of SWNTs.

PS-TuP18 Structure and Properties of Tungsten Carbide / Amorphous Hydrogenated Carbon Composite Films Prepared by Plasma Immersion Ion Immersion and Deposition, *M. Xu,* Shanghai Jiaotong University and City University of Hong Kong, *Z.W. Wu, S.H. Pu,* City University of Hong Kong, *X. Cai,* Shanghai Jiaotong University, Hong Kong, ***P.K. Chu***, City University of Hong Kong

Amorphous carbon films have excellent properties including high hardness, low friction coefficient, high chemical inertness, and good corrosion resistance. Metal-containing hydrogenated carbon films have recently attracted attention as nanocomposite films with microstructures comprising nanocrystalline grains in an amorphous matrix. These composite films have properties intermediate between a-C:H films and metal carbides and their mechanical and tribological properties and suitable for some applications. A variety of methods such as plasma-assisted chemical vapor deposition (CVD), magnetron sputtering and ion beam assisted deposition (IBAD) have been developed to produce MeC/a-C:H films. Acetylene (C2H2) plasma ion immersion implantation and deposition (PIII&D) was used in this work to fabricate carbon films with better adhesion to the substrate. Tungsten ion implantation was subsequently conducted without breaking vacuum to produce WC/a-C:H films in which there is a gradual transition region between the WC and a-C:H. The composition and structure of the films were evaluated by X-ray photoelectron spectroscopy and glancing angle X-ray diffraction. High resolution transmission microcopy was adopted to investigate the structure transformation. The surface morphology was observed by atomic force microscope and the hardness by nanoindentation measurements. Our results indicate that in addition to the formation of WC nanocrystalline grains in the amorphous structure, high energy W ion implantation reduces the sp2 contents and consequently enhancesm the mechanical properties.

PS-TuP20 Effect of Multi-polar Magnetic Field on Properties of Nano-crystalline Silicon Thin Film Deposited by Large-area Internal ICP-PECVD, ***H.B. Kim***, *H.C. Lee, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Nano-crystalline silicon films have broadly been studied due to their applications to the thin-film-silicon solar cells and the TFT(Thin Film transistor) for the elimination of light induced degradation, the enhancement of long wave length response, and high electric mobility by comparison to amorphous silicon films. Especially, the deposition of nano-crystalline with a high deposition rate at the low temperature below 200°C is important. In other to realize the nano-crystalline silicon at a low temperature, a high density plasma such as inductively coupled plasma (ICP) is required. The conventional high density plasma sources have mainly been focused on the external ICP types, however, these sources show some problems in extending to a large area due to the very thick dielectric windows and standing wave effect. On the other hand, the use of an internal type antenna where the ICP antenna is inserted into the plasma gives more feasibility in depositing nano-crystalline silicon on the large area uniformly. And the application of multi-polar magnetic field is believed to improve the properties of the deposited film. In this study, as an internal type large-area plasma source, U-type internal linear ICP source using multi-polar magnetic field utilized to deposit nano-crystalline silicon on the glass substrate (370mm x 470mm) at the temperature below 200°C using H_2/SiH_4. ICP power of 13.56 MHz is in the rage of 100 W - 4000 W and the working pressure was varied from 10 to 60 mTorr. In this presentation, the variation of physical, chemical, and electrical properties of the nano-crystalline silicon deposited by the large area internal ICP with multi-polar magnetic field will be presented as compared to the source without multi-polar magnetic field.

PS-TuP21 Study on Plasma Assisted Metal-Organic Chemical Vapor Deposition of Ti(C,N) and Zr(C,N) Thin Films and In-Situ Plasma Diagnostics with Optical Emission Spectroscopy, *J.-H. Boo, C.-K. Jung, D.C. Lim, M.C. Kim,* ***S.J. Cho,*** *J.G. Han*, Sungkyunkwan University, Korea

Ti(C,N), Zr(C,N) films were synthesized by pulsed D.C. plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) using metal-organic compounds of tetrakis diethylamido titanium and tetrakis diethylamido zirconium at 200 °C to 300 °C. H_2 and $He+H_2$ gases were used as the carrier gases to compare plasma parameter. The effect of N_2 and NH_3 gases as reactive gas was also evaluated in reduction of C content of the films. Radical formation and ionization behaviors in plasma were analyzed by optical emission spectroscopy (OES) at various pulsed bias and gas conditions. He and H_2 mixture as carrier gas was very effective in enhancing ionization of radicals, especially N_2 resulting is high hardness. However, NH_3 as reactive gas highly reduced the formation of CN radical, there by decreasing C content of Ti(C,N) and Zr(C,N) films in a great deal. The hardness of film is obtained to be 1400 HK to 1700 HK depending on gas species and bias voltage. Higher hardness can be obtained for H_2 and N_2 gas atmosphere and bias voltage of 600 V. Plasma surface cleaning using N_2 gas prior to deposition appeared to increase adhesion of films on cold forming steel. The changes of plasma including radicals and film properties are illustrated in terms of carrier and reactive gases as well as pulsed power variation.

Keywords: Ti(C,N) and Zr(C,N) films, Low temperature pulse DC-PAMOCVD, Optical emission spectroscopy, High hardness

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