

Wednesday Morning, December 14, 2016

Thin Films

Room Makai - Session TF-WeM

Plasma-based Film Growth, Etching, & Processing

Moderator: Davide Sangiovanni, Linköping University, Sweden

8:00am TF-WeM1 Flexible Electrochromic Electrodes on the Substrate of Crystalline Indium Tin Oxide with Graphene, Yekyung Kim, S.J. Lee, J.W. Seo, S.H. Han, H. Kim, Korea Electronics Technology Institute (KETI), Republic of Korea

Electrochromic technology is recently getting attention due to the requirement of the energy saving technology and the advancement of paired technology which shows synergistic effect together, such as light-responding mirrors, smart window, light shutter, etc. Nickel oxide are the most well-known anodic coloration material which is generally used as a counter electrode with enhancing coloration efficiency together with tungsten oxide, the main determinant of the coloration efficiency of whole device. The enhancement of electrochromic and cyclic stability of the electrochromic device is performed, in this study, by conditioning of nickel oxide with various methods of tungsten alloying, optimization of sputtering condition, lithiation, and so on. Also, to concrete a flexible electrochromic device, transparent conducting oxide should be deposited on a plastic substrate under the electrochromic layer. In this study, nickel and tungsten oxide were deposited on the crystalline indium tin oxide (c-ITO)/graphene/polyethylene terephthalate (PET) film. The thermally and mechanically stable graphene helps to prepare c-ITO on PET film which is hardly fabricated due to the high temperature requirement for ITO crystallization. The prepared flexible electrochromic electrodes on c-ITO/graphene/PET showed reasonable coloration performance. Also, the electrochemical and cyclic properties of electrochromic full-cell were determined.

8:20am TF-WeM2 Maximizing Retention of Complex Chemical Functionality in Plasma Polymers Via the Alpha-Gamma Transition, Andrew Michelmores, S. Saboohi, B.R. Coad, University of South Australia, Australia; R.D. Short, University of Lancaster, UK; H.J. Griesser, University of South Australia, Australia

There is increasing need for fabrication of thin polymeric films with complex chemical functionality for a variety of applications including cell therapies, biosensing, microelectronics and as platforms for surface initiated atom-transfer radical polymerization (ATRP). Conventional polymerisation techniques are not suitable in many instances as control of film thickness and topography is difficult. Plasma polymerisation is a technique which can overcome these issues, but has typically suffered from difficulty in retaining chemical structure due to fragmentation in the plasma phase and/or ion bombardment on the surface.

We have shown that pressure plays a critical role in plasma processes. By tuning the plasma from collisionless to collisional sheaths (the alpha to gamma transition) the chemistry of the plasma and the plasma polymer are drastically changed [1]; in gamma mode, the plasma chemistry is biased towards protonated precursor ions and the contribution of ions to the deposit increases. For example, we have studied deposition of ethyl α -bromoisobutyrate (EBIB) for fabricating surfaces for initiating ATRP [2]. This requires that the intact α -bromoisobutryl structure be retained on the surface of the plasma polymer. Using plasma phase mass spectrometry we show that at the transition from alpha to gamma mode protonated EBIB are formed which arrive at the surface intact and dominate the deposition process. This results in high retention of groups capable of initiating ATRP. High pressure also limits the ion energy, such that ions can be 'soft landed' and do not scramble chemical structures on the surface by ion bombardment.

More recent results on a family of ester compounds will be presented which highlight the critical roles of pressure, power and ion energy. Methods for predicting optimum conditions will also be discussed. These results open possibilities to fabricate functionalized surfaces with higher retention of chemical structure than has been possible previously.

1. Saboohi, S.; Jasieniak, M.; Coad, B.R.; Griesser, H.J.; Short, R.D.; Michelmores, A.; Comparison of Plasma Polymerization under Collisional and Collision-Less Pressure Regimes, *J. Phys. Chem. B*, 2015, 119, 15359–15369

2. Saboohi, S.; Coad, B.R.; Michelmores, A.; Short, R.D.; Griesser, H.J. Hyperthermal Intact Molecular Ions Play Key Role in Retention of ATRP

Surface Initiation Capability of Plasma Polymer Films from Ethyl α -Bromoisobutyrate, *ACS Appl. Mater. Interfaces*, 2016, 8, 16493–16502

8:40am TF-WeM3 Layer-by-layer Etching of LaAlSiO_x, Mitsuhiro Omura, K. Furumoto, K. Matsuda, T. Sasaki, I. Sakai, H. Hayashi, Toshiba Corporation, Japan

INVITED

With downscaling of metal-oxide-semiconductor (MOS) devices, high dielectric constant (high-k) oxide materials have been proposed as gate oxide, to reduce the gate leakage current. LaAlSiO_x is one of the attractive candidates. In gate transistor fabrication, removal of high-k oxide films after gate electrode etching is a critical step for the formation of ohmic contacts on source and drain regions. Dry etching is a potential process to minimize the recess of the Si substrate which leads to the degradation of device performances. The conventional approach is to use an etching process with high selectivity to the Si substrate. Sasaki et al. have achieved a high LaAlSiO_x-to-Si selectivity of 6.7 using C₄F₈/Ar/H₂ plasma [1]. Another approach to reduce the Si substrate recess is precise control of etching depth using atomic layer etching (ALE) or layer by layer etching. ALE is defined to be an etching technique that uses sequential self-limiting reactions consisting of two steps, surface modification to form a reactive layer, followed by a removal step which takes off only this modified layer keeping the underlying film intact [2]. It is reported that by ALE using an energetic Ar beam and BCl₃ gas in HFO₂ etching, drain current and leakage current characteristics of MOSFET device improved, compared with conventional reactive ion etching (RIE) [3]. To control the etching depth of LaAlSiO_x, layer by layer etching using a sequential process has been studied, focusing on the selective removal of surface modification layer and repeatability of the sequential process.

[1] T. Sasaki, K. Matsuda, M. Omura, I. Sakai, and H. Hayashi: *Jpn. J. Appl. Phys.* 54 (2015) 06GB03.

[2] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho: *J. Vac. Sci. Technol. A* 33(2) (2015) 020802.

[3] J. B. Park, W. S. Lim, B. J. Park, I. H. Park, Y. W. Kim, and G. Y. Yeom: *J. Phys. D: Appl. Phys.* 42 (2009) 055202.

9:20am TF-WeM5 Effect of Ar⁺ Ion Assist on the Properties of a-C:H Films Deposited on a Trench, Yuki Hirata, Tokyo University of Science, The University of Tokyo, Japan; K. Onishi, The University of Tokyo, Japan; S. Sasaki, Tokyo University of Science, Japan

Hydrogenated amorphous carbon (a-C:H) film have attracted considerable interest because of their high hardness, extremely low friction, high wear resistance, chemical inertness, and excellent gas barrier properties. These aforementioned characteristics make a-C:H films suitable for use in a wide range of applications such as tribological, anti-corrosional and gas barrier applications.

In our previous study, a-C:H film was prepared using the bipolar PBII&D technique on a trench-shaped target (20 mm pitch and 10 mm depth), and the coating uniformity was evaluated. In the bipolar PBII&D process, glow discharge plasma is generated by a positive pulse voltage applied to the target, and subsequently, a high-voltage negative pulse is applied for omnidirectional ion implantation and/or deposition to the target. However, this study revealed that the mechanical or structural properties of the a-C:H film differed greatly depending on whether the coating area was the top, sidewall, or bottom surface of the trench-shaped target. To reveal them, behavior of the ions or radicals around the trench-shaped target was analyzed through plasma simulation. Then it became apparent that these results were attribute to the nonuniformities of the incident flux or energy of the ions. Thus, in this study, non-reactive Ar gas was added to a toluene gas for deposition of a-C:H films to enhance the incident energy of the ions, and such ion-assisted effect was investigated simultaneously. The mechanical properties of the a-C:H film, including the internal stress in the thickness direction, were measured using a surface profilometer, the hardness and adhesiveness were measured using a nanoindentation hardness test and micro-scratch test, respectively. Furthermore, to evaluate the a-C:H film structure, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) were also conducted.

As a results, the uniformity of the film thickness was improved as the amount of introduced argon gas increased. Moreover, the hardness, internal stress, and adhesiveness were also improved in the case of an a-C:H film coated on a Si plate or at the top or bottom surface of a trench-shaped target. Such superior tendencies were considered to be caused by ion-assisted effects. On the other hand, in the case of the a-C:H film coated on the side wall, no improvement in film properties was seen. According to the Raman spectroscopy and FTIR, structure of a-C:H films were destroyed

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by Ar⁺ ion sputtering. That's why, it could be considered that Ar gas addition did not lead to the improvements for its properties but lead to the destruction of its structure.

9:40am **TF-WeM6 Characterization of PECVD a-C:H:Si:O:Cl Films**, *D. Rossi*, UNESP - Sorocaba, Brazil; *R. Landers*, Ifgw - Unicamp, Brazil; *J.R. Bortoleto*, *Steven Durrant*, UNESP - Sorocaba, Brazil

Thin films were produced by plasma enhanced chemical vapor deposition (PECVD) of tetramethylsilane, chloroform, argon mixtures. The partial pressure of chloroform in the chamber feed, C_{Cl} , was varied from 0 to 40%. Amorphous hydrogenated carbon films also containing silicon, oxygen and small amounts of chlorine, a-C:H:Si:O:Cl, were produced at deposition rates of up to about 220 nm min⁻¹ (for a C_{Cl} of 40%). Transmission infrared-analyses revealed the presence of OH groups in the chlorinated films, along with, amongst others, CH, C=C, Si-CH, Si-CH₂ and Si-O-Si groups. As revealed by X-ray photoelectron analysis, the films could be doped with chlorine to a maximum of about 2 at%. Surface morphology and roughness were examined using Scanning electron microscopy (SEM) and Atomic force microscopy (AFM). Tauc band gaps, calculated from transmission ultraviolet-visible near infrared spectra, tend to decrease from ~3.4 eV for the unchlorinated film to around 2.5 eV for those doped with chlorine.

10:20am **TF-WeM8 Plasma-assisted Atomic Layer Deposition of SiN_x Films**, *R.A. Ovanesyan*, *N. Leick*, *R.J. Gasvoda*, *J.M. Klein*, Colorado School of Mines, USA; *D.M. Hausmann*, Lam Research Corporation, USA; **Sumit Agarwal**, Colorado School of Mines, USA **INVITED**

The introduction of 3-D device architectures in integrated circuits has created a need for atomic layer deposition (ALD) of highly conformal ultra-thin films. In particular, ALD of low-dielectric-constant, carbon-containing silicon nitride (SiC_xN_y) films at temperatures ≤400 °C is required. However, controlled incorporation of C atoms into SiN_x during ALD remains challenging. In this work, we report the C incorporation mechanism during two plasma-enhanced SiC_xN_yALD processes. The first ALD process consisted of three steps, Si₂Cl₆/thermal CH₃NH₂/N₂ plasma, while the second process consists of two steps, Si₂Cl₆/CH₃NH₂ plasma. In both ALD processes, we have determined the film composition, reactive sites, and adsorbed surface species using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. In addition, the growth per cycle (GPC) and refractive index were determined using *in situ* four-wavelength ellipsometry.

Our IR spectra show that in the first ALD process, the CH₃NH₂ thermally reacts with -SiCl_x surface species created after the Si₂Cl₆ half-cycle to form -CH_x terminated surface amides. During the subsequent N₂ plasma half-cycle, in addition to nitridation of Si, a fraction of the surface CH_x groups were incorporated into the SiC_xN_y film as -N=C-N- species, which appear as a strong vibrational mode at ~2170 cm⁻¹. The composition of the SiN_x films in the two-step ALD process was very similar, with C incorporated primarily as -N=C-N- groups created during the CH₃NH₂ plasma half-cycle. We find that during the exposure of the film to Si₂Cl₆ following a CH₃NH₂ plasma half-cycle, surface carbodiimides (-N=C=NH) react to nitriles (-NH-C≡N), while most of the surface is terminated with -SiCl_x species. The subsequent CH₃NH₂ plasma half-cycle, shows that the -NH-C≡N species formed during the Si₂Cl₆ half-cycle are removed, and the N=C=NH surface species are restored along with -NH_x groups. For the Si₂Cl₆/CH₃NH₂ plasma ALD process, SiN_x films grown at 400 °C show a carbon content of ~4 at.% as measured through Rutherford backscattering spectroscopy combined with hydrogen forward scattering. Transmission electron microscopy shows a conformality of >95% for the SiC_xN_y films. The GPC for both processes was ~0.9 Å, with a refractive index of 1.95 and 1.86 for the N₂ plasma and CH₃NH₂ plasma ALD processes, respectively.

11:00am **TF-WeM10 Atomic Scale Analyses of Plasma Surface Reactions using Molecular Dynamics Simulations and Ion/radical Beam Experiments**, *Satoshi Hamaguchi*, *H. Li*, *T. Ito*, *M. Isobe*, *K. Karahashi*, Osaka University, Japan

As the sizes of semiconductor devices continue to diminish and are now approaching atomic scales, the downsizing of transistors following Moore's law is bound to end in the near future. However, the continuing market demand for higher performance and lower energy consumption of large-scale integrated (LSI) circuits has driven a series of innovations in device technologies, such as three-dimensional (3D) device structures and devices based on non-silicon materials. Manufacturing of these non-conventional devices also poses new challenges for processing technologies. For example, magnetic materials used in magnetoresistive random-access memories (MRAMs) cannot be etched efficiently by the existing reactive ion etching (RIE) technologies, which has so far limited the level of

integration of MRAM devices. The modern near-atomic-scale devices also require atomic level precision in their manufacturing processes, which has also driven new technologies such as atomic layer deposition (ALD) and atomic layer etching (ALE). In this work, we have developed analytical techniques to examine plasma-surface interactions at the atomic scale using molecular dynamics (MD) simulation and multi-beam (i.e., ion and radical beam) injection experiments [1], in order to understand atomic layer reaction mechanisms that largely determine efficiencies of such atomic-level processing technologies. Some of our recent analyses include surface chemical reactions for magnetic materials [2,3] metal oxides [4], Si-based materials [5] as well as damage formation mechanisms [6,7] due to ion bombardment during RIE processes.

References

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- [7] K. Mizotani, M. Isobe, M. Fukasawa, K. Nagahata, T. Tatsumi and S. Hamaguchi, J. Phys. D: Appl. Phys. 48 (2015) 152002.

11:20am **TF-WeM11 Low-temperature Fabrication of Amorphous Zinc Tin Oxide Thin Film Transistors without Annealing Process**, *Sungmin Kim*, *J.M. Kim*, *H.J. Kim*, Seoul National University, Korea, Republic of Korea

Amorphous oxide semiconductor (AOS) such as InGaZnO_x (IGZO) and ZnSnO_x (ZTO) attracts an attention as a new channel material for thin film transistors (TFT). It has outstanding properties such as high field effect mobility (>10cm²/V-s) as well as transparency and uniformity. Therefore, display industry has named it as a prime candidate of channel material for large-sized and flexible display devices. However, considering that substrates in use for flexible display devices are polymer materials like PEN or PI, AOS has a critical drawback that it requires annealing process over 350°C. This is a quite low temperature compared to conventional silicon-based process (over 800°C), but the process temperature must be under 200°C to prevent deformation of polymer substrates.

In this study, the fabricated ZTO TFTs have a ZTO bottom gate and ITO top contacts, and all of them were made by RF magnetron sputtering system. And we replaced post annealing step with heating up the sputter stage up to 200°C during sputtering and forming 10% oxygen atmosphere. Electrical properties such as threshold voltage (V_{th}), mobility and subthreshold swing (SS) of ZTO TFTs were compared to convince that our new process could replace post annealing over 350°C. Analyses for morphology and chemical compositions are also conducted.

Saturation mobility of ZTO TFTs with 350°C annealing process and with our novel process were measured to be 17.4 and 11.7cm²/V-s, respectively. Post annealing at 200°C cannot activate ZTO TFTs at all, but by heating up the sputter stage, heating of 200°C was sufficient to activate TFTs. There was a little reduction of mobility, but 11.7cm²/V-s is still good enough giving that mobility of 10cm²/V-s is enough for large sized display (>70 inches). And SS values of 350°C annealed sample and one sputtered at 200°C was 0.31V/decade and 0.50 V/decade, respectively. Also, chemical composition and surface roughness was analyzed by XPS and AFM. These results also show that our new low temperature process is suitable for manufacturing AOS TFTs.

The main reason of this phenomenon can be served by combination of plasma and thermal energy in sputter chamber. Generally, it is obvious that as-deposited AOS channel needs oxygen curing to connect broken bonds between metal and oxygen atoms. While Ar/O₂ plasma in sputter chamber redeems relatively low thermal energy (200°C), curing reaction immediately occurs on as-deposited ZTO. Consequently, we made ZTO TFTs below 200°C process, rather than post annealing over 350°C. Performances of them were still applicable for next generation display. But it shows a little bit poor performance, so there must be further study to advance properties

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