ALD Fundamentals
Room 113-115 - Session AF2-WeM
Plasma ALD II

Moderators: Markku Leskela, University of Helsinki, Finland, Jihwan Ahn, Seoul National University of Science and Technology

10:45am **AF2-WeM-12 Low-Temperature Plasma-Enhanced ALD of Highly Conductive Niobium Nitride Thin Films with RF Substrate Biasing**, ***Yi Shu***, *A O'Mahony,* Oxford Instruments Plasma Technology*; H Knoops,* Oxford Instruments Plasma Technology, UK*; A Kurek,* Oxford Instruments Plasma Technology*; T Miller,* Oxford Instruments Plasma Technology, UK*; O Thomas, C Hodson,* Oxford Instruments Plasma Technology

Low-temperature superconductivity of Niobium Nitride (NbN) enables the utilization of NbN thin films in numerous quantum information applications. Recently, plasma-enhanced ALD (PEALD) of NbN thin films has been studied extensively[1,2,3], aiming for high quality NbN thin films deposition with precise thickness control at low process temperature (e.g. <400°C). These processes still require a long plasma exposure time (>40 s) and relatively-high deposition temperatures (>300°C) to eliminate impurities for the optimum film properties, such as high superconducting transition temperature (T_c) and low normal-state resistivity. On the other hand, it has been shown that RF substrate biasing applied during PEALD deposition can increase ion energy and influence film properties including stress[4], crystallinity[5], density[6], and resistivity[7]. Following above results, bias-enhanced PEALD of NbN thin films deposition with (t-butylimido)-tris(diethylamido) niobium (TBTDEN) and remote H_2/Ar plasma is investigated in this work.

This study was carried out in an Oxford Instruments Plasma Technology FlexAL ALD tool equipped with an RF-biased table (13.56 MHz, substrate biasing up to 100 W power, -350 V resulting DC bias voltage), where independently controlled RF substrate biasing was applied along with mixed H_2/Ar plasma generated by inductively-coupled plasma (ICP) RF power. Coupons of silica samples were used as substrates. Film quality was evaluated by film resistivity at room temperature (RT), which was calculated from sheet resistance measured by the four-point probe method (FPP), and film thickness measured by ex situ spectroscopic ellipsometry (SE).

Different plasma parameters were investigated, e.g. RF bias power ranged from 0-75 W, and plasma duration ranged from 10-50 s. Benefit from the RF biasing, RT resistivity as low as 142 μΩ*cm was observed with NbN thin films deposited at 250°C, by PEALD process with a 20 s plasma exposure time. Moreover, such conductivity, which is corresponding to high superconducting transition temperature (T_c) [1], was found to remain with films grown at lower process temperatures down to 120°C.

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[3] *Hinz et al*., *Supercond. Sci. Technol.* **25** *075009*(2010)

[4] Profijt *et al*., *J. Vac. Sci. Technol. A*. **31** 01A106 (2013).

[5] Ratzsch *et al*., *Materials* **8**, 7805-7812 (2015).

[6] Profijt *et al*., *Electrochem. Solid-State Lett*. **15**, G1-G3 (2012).

[7] Faraz *et al*., presented at AVS ALD2017(2017).

11:00am **AF2-WeM-13 Low-temperature Plasma Assisted Atomic Layer Deposition of Cadmium Telluride**, ***James Pattison***, University of Maryland*; B VanMil, A Hewitt,* U.S. Army Research Laboratory*; N Strnad,* University of Maryland*; Y Chen, P Wijewarnasuriya,* U.S. Army Research Laboratory

Cadmium telluride (CdTe) is an important group II-VI semiconductor that can be alloyed with the semi-metal HgTe to create $Hg_{1-x}Cd_xTe$ (MCT) based semiconductor materials, with a band gap tunable from 0 to 1.5 eV. MCT is the incumbent technology used in long-wave infrared (IR) imaging. Surface passivation is critical for the next generation of infrared focal plane arrays (FPAs) used for imaging in the long-wave infrared (8-12 mm band). As device dimensions decrease in newer FPA designs, the surface area to bulk volume ratio increase, and the surface recombination of charge carriers in MCT photodiodes can limit the performance of FPAs, ultimately degrading the diode signal-to-noise ratio. CdTe is an ideal passivation material for MCT due to being very close in lattice match to $Hg_{0.78}Cd_{0.22}Te$ (band gap of 115 meV equal to 10.6 mm), having similar thermal expansion coefficient, and being transparent to long wave infrared. The high-aspect ratio features present in next-generation FPAs present a challenge to current state of the art CdTe passivation by molecular beam epitaxy, which deposits material in a line-of-sight fashion. Atomic layer deposition of CdTe provides conformal coverage of these features with atomic-level thickness control, overcoming this challenge. The temperature of any MCT processing step, including passivation, must occur at low enough temperatures to avoid outgassing of mercury from the MCT device, which is catastrophic to performance. Past work on CdTe ALD and CdTe MOCVD has relied upon thermal deposition processes (> 220°C) that are incompatible with MCT device processing. Here we present preliminary results from our novel plasma-assisted ALD process for deposition of CdTe on silicon and MCT device substrates at a variety of temperatures (from 50 to 200°C) compatible with MCT device processing. Optical characterization by dynamic in-situ spectroscopic ellipsometry (iSE) during growth provides growth-per-cycle and insight into the nucleation and deposition mechanisms. X-ray photoelectron spectroscopy (XPS) confirms the presence of CdTe and examination of other contaminants within the ALD film. X-ray diffraction was used to study the orientation of ALD films on both HgCdTe and silicon substrates. Transmission electron microscopy was used to characterize the film thickness, orientation, and chemistry.

11:15am **AF2-WeM-14 Improved Deposition Rate of Low T PEALD Silicon Nitride Using Amines**, ***Sungsil Cho***, *S Chang, J Park,* Entegris Inc., Republic of Korea*; B Hendrix, T Baum, J Giolitto,* Entegris Inc.

Plasma-enhanced atomic layer deposition (PEALD) of silicon nitride (SiNx) films using silicon-halide precursors and plasma-activated ammonia (NH_3) is well-known and characterized. In this presentation, we dramatically improved the efficiency of the process by catalyzing the precursor dose with an amine. Specifically, hexachlorodisilane (Si_2Cl_6) and tetrabromosilane ($SiBr_4$) were used to deposit SiN films via plasma-activated NH_3 at a deposition temperatures from 250-450°C. The deposition rate was increased 2-3X by modifying the pulse sequence, as shown in Figure 1.

The results of amine catalyzed PEALD-SiNx films were compared to conventional PEALD-SiN films. Figure 2-A shows that the growth rate of the NH_3 catalyzed PEALD-SiN film from Si_2Cl_6 saturated at 2.8~3.0 Å/cycle; this was 2~3 times higher growth rate than the normal PEALD-SiN film (~1Å/cycle) process. This increase may be attributed to the amine catalyst leading to a lower activation energy, influencing the surface reaction of the Si compound. A similar 2X enhancement in growth rate was observed for $SiBr_4$.

In terms of the characterization of the amine catalyzed PEALD-SiN film, we found that the wet etch rate (WER) of the amine catalyzed PEALD-SiN film was generally higher than that of the normal PEALD-SiN film process. The WER of the SiN film was improved as plasma exposure time or plasma power was increased. Furthermore, the amine catalyzed PEALD-SiN film showed excellent conformality on silicon oxide trench structures with high aspect ratios (AR~11:1), as shown in Figure 3-A. We also observed that the SiN film was uniformly etched down the sidewall and at the bottom of the via structure.

11:30am **AF2-WeM-15 Improved Adhesion and Electrical Properties of Plasma-Enhanced ALD Platinum through Cycle-by-Cycle Hydrogen Plasma Treatment**, ***Martin Winterkorn***, *J Provine, H Kim, P Schindler, T Kenny, F Prinz,* Stanford University

Insufficient adhesion of platinum thin films to their underlying substrates is a cause of concern in many applications such as biomedical and MEMS devices. We report on significantly improved adhesion of plasma-enhanced ALD platinum films on multiple substrates through in-situ cycle-by-cycle hydrogen plasma treatment. Further, we demonstrate a novel method for quantifying adhesion, which involves the deposition of a highly stressed overlayer and a subsequent liftoff procedure. The effect of the hydrogen plasma treatment on film resistivity and uniformity have also been characterized, and an extreme substrate dependence has been observed, with the most extensive treatment condition resulting in a 8% decrease in resistivity compared to no treatment on Al_2O_3 substrates, but a 78% increase on SiO_2 substrates.

All films were deposited at 270°C in an Ultratech / Cambridge Nanotech Fiji ALD reactor, using trimethyl(methylcyclopentadienyl)platinum(IV) as the precursor and remote O_2 plasma as the oxidant, with 400 cycles resulting in approximately 20 nm thick films as confirmed by X-ray reflectivity measurements. The plasma treatment consisted of an additional 10 seconds of H_2 plasma and 10 seconds of O_2 plasma after each cycle, with purge times of 5 seconds. Various conditions were investigated, performing the treatment during all 400 cycles, only the first 200 cycles, only the first 50 cycles, or not at all (numbers 4 through 1, respectively).

Adhesion was evaluated using tape lift-off, and a novel method that mimics real application in MEMS fabrication processes: Two-layer photoresist is patterned with arrays of squares of various sizes on top of the platinum film, followed by e-beam evaporation of a 200 nm thick Pt layer which has a high tensile stress of 640 Mpa. A lift-off procedure is then carried out on the sample, which includes submerging it in solvents and ultrasonic agitation. In case of insufficient adhesion, individual patterned squares delaminate at the interface between the ALD platinum layer and the substrate. The fraction of delaminated squares at various sizes, as observed by optical microscopy, can then be used as a quantitative indication for adhesion strength.

11:45am **AF2-WeM-16 Low Temperature SiNx Film Deposition by Plasma Enhanced Atomic Layer Deposition with Trisilylamine***, **Sun Jung Kim**, S Yong, Y Choi, H Hwangbo, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Recently, the degree of integration density of semiconductor devices is continuously increasing and critical dimension (CD) also is reduced to less than 20nm. In the nanoscale devices, silicon nitride (SiN_x) layers are essential and critical for the fabrication of nanoscale devices and it is important to control SiN_x film thickness at atomic level. Atomic layer deposition (ALD) processes are applied for the atomic layer thickness control. It is also known that the low process temperature for SiN_x film deposition less than 400°C is becoming an issue in ALD processes maintaining growth per cycle (GPC) of 1.0Å/cycle or above [1].

In this study, we developed SiN_x plasma-enhanced atomic layer deposition (PEALD) films with trisilylamine (TSA) as a Si precursor and NH_3 in inductively coupled plasma (ICP) reactor for low temperature deposition high GPC. Reactive radicals and ions are generated in ICP environment and make low temperature processing possible. The GPC was measured as high as 1.2Å/cycle at 350℃ of substrate temperature. The ratio of nitrogen and silicon (N/Si) was determined as high as 1.33 at an optimized condition. We also investigated chemisorption path of TSA on SiN_x film during first-half reaction of PEALD process with a reference of adsorption analysis of TSA on Si (100) surface [2].

References

[1] X. Meng, Y. Byun, H. S. Kim, J. S. Lee, A. T. Lucero, L. Cheng and J. Kim, Materials, Vol. 9, No.12, pp. 1007 (2016).

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