Ishikawa, M. Hori, Miyoshi, K. Kawamura, M. Izawa, of W, TiN, and SiN

Selectivity Control in Annealing Procedures for Rapid Thermal Process requirements. This work is partially supported by the Naval compared with plasma diagnostics to gain a better understanding of the particular attention paid to the etch rates, selectivity (vs. car

we will discuss the processing of monolayer material systems such as these features to the processing of select materials systems. Specifically, characterization techniques and demonstrate how the applicability of demonstrate this precise level of control and in reactive gas backgrounds, a relatively low radical production rate beam electronics will require control over radical to

laye

Processing with atomic layer precision requires the ability to not only add, plasma etching processes, which are cyclic repetitions of plasma exposure and infrared annealing was repeated ten times.

Annealing was repeated ten times.

PS+EM+TF

10 sec. The etched amount per cycle for W increased with the annealing time and saturated when the annealing time exceeded 20 sec. The etched amount per cycle for SiN saturated when the annealing time exceeded 15 sec. These results imply that the ALE process for W, TiN, and SiN are self-limiting in nature. Moreover, by choosing an optimal infrared annealing time, both highly selective and nonselective ALE for different materials was obtained. For instance, infinitely selective ALE of W over TiN was achieved when infrared annealing time was 8 sec. [1] K. Shinoda et al., J. Phys. D: Appl. Phys. 50, 194001 (2017).


9:00am PS+EM+TF-ThM4 Mechanisms for Atomic Layer Etching of Metal Films by the Formation of Beta-diketone Metal Complexes, Tomoko Ito, K. Karashishi, S. Hamaguchi, Osaka University, Japan Ar ion milling processes have been widely used for the fabrication of magnetic tunnel junctions (MTJ) of magnetoresistive random access memory (MRAM) devices. However, Ar ion milling has a problem of surface damage caused by high energy ion bombardment, so the development oflow-energy reactive ion etching (RIE) processes is imperative for further miniaturization of MTJ cells. In recent years, beta-diketonates such as acetylacetone (acac) andhexafluoroacetylacetone (hfac) have been considered as efficient etchants for thermal atomic layer etching (ALE) of metal films by the formation of volatile beta-diketonate metal complexes. Moreover, if low-energy ion incidence, rather than heating of the substrate, enhances the formation of organic metal complexes and their desorption from the metal surface, anisotropic ALE of metal films may be achieved. In this study, we explore the possibility of the development of such ion-enriched metal surface etching using surface reactions of beta-diketonates. The objectives of our research are, therefore, to understand surface reactions between gas-phase beta-diketones and metal surfaces and to clarify the beam-surface interaction between low-energy Ar ions and beta-diketone adsorbed metal surfaces. To achieve these objectives, we have developed an atomic layer process (ALP) surface analysis system, which consists of a high-resolution X-ray photoelectron spectroscopy (XPS) analysis chamber and an ALP reaction chamber. The system allows in-situ analyses of, e.g., acac orhfac adsorbed Cu, Ni and Co surfaces and those after an exposure to low-energy Ar or Xe ion fluxes. The typical reactive gas exposure was in the range of 100 -10000 L (in units of L: Langmuir: 10^-6 Torr·s) and the ion energy was in the range of 10– 50 eV. It is found that, for pre-oxidized Ni and Cu surfaces, hfac molecules adsorbed without C-O and C-F bond braking. It is also found that low-energy Ar ion injection breaks down adsorbed hfac molecules even on a pre-oxidized Ni surface, fluorinating the Ni surface. The results show the difficulty of using low-energy ion exposure to enhance the formation of volatile metal complexes but also suggests a possibility of atomic-level surface modification of metal films using organic molecules, which may be used for highly controlled etching processes.

9:20am PS+EM+TF-ThM5 Thermal Atomic Layer Etching of Transition Metal Films, Charles Winter, Wayne State University

INVITED

Atomic layer deposition (ALD) features self-limiting growth, which affords inherently conformal coatings on shaped substrates and Ångstrom-level thickness control.1 Atomic layer etching (ALE) is a related technique, where layers in a film are removed one layer at a time and involve a self-limited mechanism.2 Until recently, almost all ALE processes entailed either plasmas or ion beams.3 Plasmas and ion beams require expensive equipment and the energetic species may damage sensitive layers in films. As a result, there is considerable interest in the development of purely thermal atomic layer processes that use chemical reactions to achieve thickness reductions. The first thermal ALE processes were only reported in 2015 for metal oxides and fluorides,4,5 and many materials can now be etched thermally. Cobalt, copper and other first row transition metal films have wide applications in microelectronics devices.6 The ability to carry out ALE on these metals would be very valuable. However, there has been little progress reported to date in the thermal ALD of first row transition metal films. We recently reported the ALD growth of cobalt7 metal films and have explored these films as starting substrates in thermal ALE. In this talk, we will give an overview of the thermal ALE of cobalt metal films. These processes entail treatment of the cobalt metal films with formic acid in a first step, presumably to afford surface layers of cobalt(II) formate. These oxidized surfaces are then etched using various etchants in a second step to afford volatile cobalt(II) complexes, resulting in etching. Ligands that can be used to promote etching will be overviewed. Thermal ALE of copper and other metal films will also be presented.

In our presentation, we will present our investigation of the usage of a gas cluster ion beam (GCIB) under organic vapor to irradiate a surface to produce atomic layer etchings (ALE). Gas cluster ions are aggregates of thousands of atoms or molecules that are collectively ionized and can be focused into a GCIB. The kinetic energy of a gas cluster ion is shared between the thousands of gas atoms or molecules; hence, the energy per particle in the cluster can be easily reduced to several eV. Furthermore, gas cluster ions can transfer a relatively large amount of energy to a concentrated area of the target surface; thus, a large number of target atoms can be sputtered by one gas cluster ion. As a result of the high-energy impact of gas cluster ions, low-damage surface modification takes place. Because of the features outlined above, GCIB guns are also widely used in conjunction with surface analysis techniques such as secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS).

Because gas-cluster ions deposit energy in a condensed manner without severe damage, surface reactions are enhanced even at room temperature, which is beneficial for ALE. In our study, we performed halogen-free ALE of Cu using oxygen-GCIB irradiation under acetic acid vapor. We performed the etching process in the following steps: (1) adsorption of acetic acid on Cu, (2) evaporation of residual acetic acid vapor, and (3) reaction between acetic acid and Cu with the subsequent removal of the surface Cu layer via oxygen-GCIB irradiation. During one cycle of ALE, a very thin layer of acetic acid was adsorbed onto the Cu. Subsequently, the chemically altered Cu on the surface layer was removed with oxygen GCIB irradiation. When the Cu surface was irradiated with a 20 kV oxygen GCIB, Cu atoms beneath the surface layer were also sputtered after the removal of the chemically modified layer and as a result, this etching process was not self-limiting. On the contrary, when the surface was irradiated with a 5 kV oxygen GCIB, Cu atoms beneath the surface layer were not sputtered after the removal of the chemically modified layer. Thus, it could be concluded that halogen-free ALE could only be achieved at a lower oxygen GCIB voltage, namely 5kV. In the presentation, we will report the preliminary results of the various metal etching experiments we conducted with a GCIB under organic vapors and report their applications for ALE.


Thursday Morning, October 25, 2018


Atomic layer etching (ALE) applies sequential deposition and etching steps with short processing step length to establish sputter-free layers. ALE and etching of SiO2 selective to Si, SiN, and SiGe. For continuous plasma etching, process gas mixtures, e.g., C2F6/H2, have been employed and enable highly selective material removal based on reduction of the fluorine content of deposited steady-state HFC films. This approach, however, is not successful for ALE since the residual hydrogen during reaction steps will induce etching and reduce the remaining thickness of the deposited HFC film. This HFC film on the surface is required for both etching of SiO2 and passivation of the SiN, Si, and SiGe, and a reduction in film thickness leads to lower material etching selectivity. C2F4 with hydrogen reduces fluorine content in the precursor structure and allows deposition of fluorine-deficient HFC films without suppressing the formation of the passivation layer on the surface. Our results support that gas pulsing of complex HFC precursors in ALE provides a new opportunity of utilizing the precursor chemical structure for achieving near-atomically abrupt selective ALE processes for SiO2 over SiN, Si, SiGe, and potentially for other materials. The authors gratefully acknowledge financial support of this work by the Semiconductor Research Corporation (2017-NM-2726).
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