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Sacrificial layers for air gaps in NEMS using alucone molecular layer deposition☆

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ABSTRACT

A molecular layer deposition approach is reported that produces a new class of hybrid organic–inorganic thin films. These films have very low densities, and display typical atomic layer deposition characteristics: controllable linear growth, conformality, low roughness, and uniform composition. Because of their aluminum content, the alucone films cannot be dry etched with oxygen plasma. In accordance with their molecular structure, the new materials are completely removed in hydrochloric acid solutions. Since they can be etched with accurate control in acidic solutions, these hybrid materials are promising for the fabrication of MEMS/NEMS (Micro/Nano Electro Mechanical Systems) devices. Doubly supported structures with 120 nm air gaps are demonstrated using alucone materials as sacrificial layers.

1. Introduction

Sacrificial layers are widely used in micro- and nano-surface micromachining processes for the fabrication of MEMS and NEMS devices capable of both in and out of plane motion. The purpose of a sacrificial layer is to create gaps between features. These gaps serve varying purposes depending on the device such as: allowing mechanical functionality; separating charge between surfaces; and creating thermal isolation. A great variety of materials are used as sacrificial layers, ranging from a broad selection of metals, to ceramics and polymers. There are several commonly employed methods for deposition of sacrificial layers: physical vapor deposition (PVD); chemical vapor deposition (CVD); and polymer spin casting [1]. Each of these methods has made the leap from micro to nanofabrication [2–5].

PVD evaporation by thermal or electron beam heating allows for controlled thin-film deposition of most metals. Tanner and Rogers have successfully fabricated cantilever devices with integrated tunnel junctions employing a 60 nm sacrificial layer of Al deposited by electron-beam evaporation on top of 250 nm electrodes [6]. CVD produces near conformal films that tend to yield rounded corners and dimples when deposited on top of existing features [7]. Recently Kim et al. produced a 10 nm thick, continuous, dense and conformal layer of Cu having an RMS roughness of ~1 nm [8]. Choi et al. were able to create spacers for nanoscale CMOS technology using 10–30 nm thick LPCVD deposited PSG sacrificial layers, but reported only 70% step coverage over a feature having a thickness of 20–30 nm [3]. Kaul et al. demonstrated that a 200 nm thick layer of silicon dioxide deposited by PECVD could be thinned down to 20 nm and used as a sacrificial layer for electromechanical carbon nanotubes switches [4].

The methods introduced for deposition of sacrificial layers for use in the development of MEMS or NEMS devices all face serious limitations as the layers approach nanoscale thickness. One difficulty with PVD evaporation is its poor step coverage. Because of geometrical shadowing caused by existing structures, the resulting thin film will be preferentially deposited on the top and top corners of the existing features. Consequently, the step coverage is particularly poor at the bottom corner of trenches and vias [9]. The ratio of film feature thickness to gap width of existing features limits the application of PVD deposited sacrificial layers. Oblique angle physical evaporation can significantly improve the step coverage limitations of PVD evaporation [9]. In addition, PVD sputtering typically allows for better step coverage than evaporation and a larger selection of materials such as ceramics [10].

The CVD method also has several limitations. CVD offers better step coverage than PVD techniques but the process cannot produce

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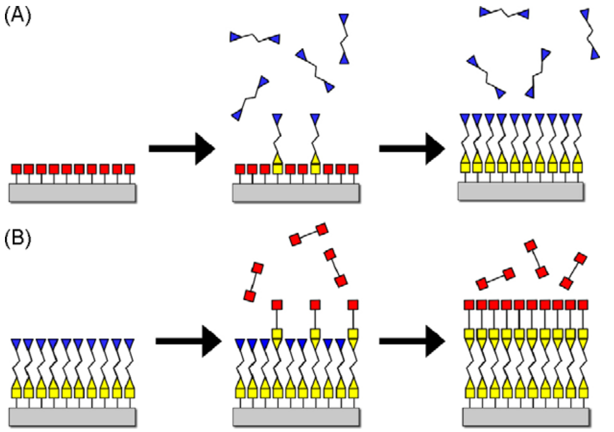

Fig. 1. Schematic of the binary MLD process. Each molecule is represented by a backbone with two reactive chemical groups at each end. The squares and triangles represent two different chemical groups.

ideally conformal thin films. In addition, many CVD processes are conducted at high temperature. High temperature limits use of patterning materials such as resists, and induces thin film stress that may be deleterious to device performance. Spin-coated polymers can also be employed as sacrificial materials. Spin-coating is a simple and low temperature process. However, spin-coated polymer films suffer from poor step coverage. Precise control of the film thickness is also very difficult.

Atomic layer deposition (ALD) is a thin film direct-growth process that can circumvent all the aforementioned limitations of PVD and CVD methods when implemented at low temperatures. ALD is a thin film deposition technique that produces accurately controlled, dense inorganic films at low processing temperatures. ALD is based on sequential, self-limiting reactions [11,12]. Since the reactions are self-limiting, the ALD films are pinhole free and can be grown with accurate control in high aspect ratio structures [13–15]. ALD thin films have been used previously in the fabrication of MEMS devices. Al_2O_3 ALD has been used as a micro-/nano-scale structural material [16–18] and as protective and wear resistant coating in MEMS devices [19,20]. ALD has also been used to produce sacrificial layers of 10 nm to fabricate lateral nano-gaps [21].

Molecular layer deposition (MLD) is an extension of ALD and can deposit organic materials [22–24]. As shown in Fig. 1, MLD deposits organic molecular fragments during each reaction cycle. While ALD films are usually binary inorganic materials, MLD films can be entirely organic or hybrid organic/inorganic materials. Early work focused on homobifunctional organic precursors that form purely organic films using alternating condensation reactions [22–24]. More recent work has focused on combining homobifunctional organic and inorganic reactants to create hybrid organic/inorganic materials [25]. The most recent efforts employ the use of heterobifunctional and ring-opening organic reactants to create a new class of hybrid MLD materials [26].

Two systems of hybrid organic/inorganic MLD materials are reported in this paper. First is a binary system, where two precursors are used: an inorganic reactant, trimethylaluminum (TMA) and an organic reactant, ethylene glycol (EG). This hybrid system produces polymeric aluminum alkoxides, or alucones [25]. Due to its binary nature, this system will be referred to as the “AB” alucone system. The second MLD system uses three reactants: an inorganic molecule, TMA, a heterobifunctional organic molecule, ethanolamine (EA), and a ring-opening molecule, maleic anhydride (MA) [26]. This new approach requires three steps, and the obtained hybrid organic/inorganic film is referred to as the “ABC” alucone system. The extension to three-step ABC MLD processes expands the variety of reactants and compositional diversity that can be achieved with MLD.

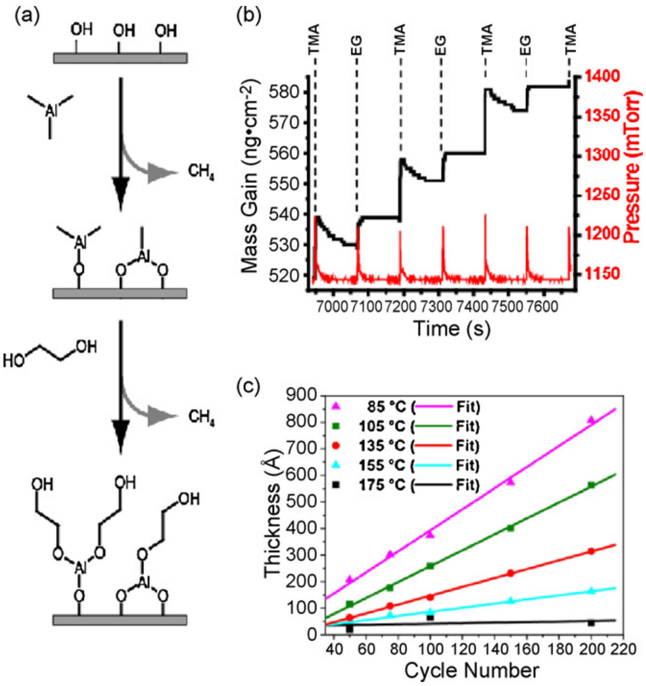

Fig. 2. Surface chemistry and growth characteristics for the AB alucone system: (a) schematic of the reaction mechanism, (b) quartz crystal microbalance mass gains during TMA and EG exposures, and (c) linear growth vs. number of cycles for various growth temperatures as measured by X-ray reflectivity.

2. Results and discussion

2.1. AB alucone growth

As illustrated in Fig. 2a, the AB alucone growth is a binary self-limiting process [25]. The initial exposure to trimethylaluminum leads to a reaction with the –OH hydroxyl species on the surface. At the end of this reaction, when all the hydroxyls are consumed, the surface functionality is changed entirely from hydroxyl to $-AlCH_3$ methyl species. After a purge of the extra reactants and byproducts, the surface is exposed to ethylene glycol. One hydroxyl end of this molecule reacts with the $-AlCH_3$ methyl species, producing an aluminum alkoxide on the surface. The other end of the molecule regenerates the hydroxyl terminated surface. After all the $-AlCH_3$ methyl species have reacted, a purge step removes the extra reactants and products. Because the newly formed surface has the same hydroxyl functionality as the initial surface, the process can be repeated in a cyclic fashion.

Fig. 2b displays the mass gains during TMA and EG exposures for steady state growth recorded by the *in situ* quartz crystal microbalance (QCM) at 135 °C. Details about the experimental setup have been given elsewhere [27]. The decrease in mass gain after the TMA exposure occurred over a period of 60–90 s. This long progressive decrease is much longer than the time required for the pressure to return back to the baseline pressure. Mass gains with decreases of this type have been observed previously during Al_2O_3 ALD on polymers and are attributed to the diffusion of some of the TMA out of the polymer [28].

Ex situ X-ray reflectivity (XRR) scans confirmed the linear growth of alucone films versus number of cycles over a wide range of temperatures [25]. As shown in Fig. 2c, the alucone growth rates were inversely proportional to the growth temperature. Growth rates varied between 4 Å per cycle at 85 °C and 1.7 Å per cycle at 135 °C. The growth rates measured with XRR agreed with *in situ* results from the QCM. Although the growth rates varied inversely propor-