ATOMIC LAYER ETCHING OF SUSPENDED ULTRA-THIN STRUCTURES

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ABSTRACT

We performed the first-ever demonstration of atomic layer etching (ALE) on suspended nano-devices, which were fabricated using an atomic layer deposition (ALD) on polyimide process [1]. Two thermal ALE chemistries including Sn(acac)₂/HF and TMA/HF, were used to remove Al₂O₃ from suspended microbridges and microbolometer-type absorption structures [2], [3]. Measurement of the thermal time constants of several microbridges after ALE was used to evaluate finite Al₂O₃ material removal. ALE is currently limited to transistor processing, but will have substantial influence on a wide variety of microdevices. Here, we demonstrate ALE's functionality for the fabrication of ultra-thin suspended structures.

KEYWORDS

Atomic layer etching, thin film, atomic layer deposition, nano-fabrication, micropulse calorimetry

INTRODUCTION

ALE has been identified as one of the leading low damage process technologies for future transistor development and will offer unique opportunities for nano- and micro-device fabrication [4]. As device thicknesses continue to shrink to several nanometers, precise etching processes for successful device fabrication will be required. Additionally, the stringent demands of precise tolerances for 3-dimensional finFET devices require extremely precise, low-damage etching processes. Current plasma processing approaches expose devices to large particle fluxes causing damage to surfaces. While there are currently no records of ALE for micro and nano electro-mechanical systems (N/MEMS) it is expected to permeate the field with unique utility for specific fabrication processes.

Similar to ALD, thermal ALE consists of self-limiting, conformal, and atomically precise layer by layer removal of material through thermodynamically favorable vapor phase reaction cycles. However, while in principle, ALE can be thought about as ALD in reverse, it is not a simple reversal of the chemical reactions. Different precursors must be used in the removal of material. The majority of ALE to date (non-thermal) has used ion-enhancement or energetic neutral atom beam enhanced surface reactions together with halogenation of the surface to etch the material [5]–[8]. These techniques may provide anisotropic etching for given applications. Recently, thermal ALE has been demonstrated based on spontaneous thermal chemistries. For example, etching of Al₂O₃ may be achieved by an initial precursor fluorinating the surface to form a metal fluoride layer. The second metal precursor can then accept fluorine from the metal fluoride and donate a ligand to the metal in the metal fluoride to form volatile species through a ligand-exchange process. For example, the removal of Al₂O₃ is achieved using tin(II) acetylacetonate (Sn(acac)₂) and HF as the reactants [2]. The overall reaction is:

Figure 1. General schematic of Al₂O₃ ALE surface chemistry using Sn(acac)₂ and HF [9]. (Step A) The surface of Al₂O₃ is converted to an AlF₃ surface layer through a fluorination reaction. (Step B) The metal fluoride layer exchanges ligands with the Sn(acac)₂ producing volatile species which removes the AlF₃ surface layer.

A schematic showing the individual Sn(acac)₂ and HF reactions is given in Figure 1. The metal fluoride ligand exchange mechanism for etching may be extended to other chemistries as well, including trimethylaluminum (TMA) and HF [3].

ALD technologies have provided an extreme utility by offering conformal coatings for 3-dimensional structures. For example, underside coating of suspended MEMS cantilevers provided superior anti-stiction coatings [10]. The ability to remove material by single atomic layers conformally on 3-dimensional structures will also offer extreme control in many etching processes for N/MEMS. As an example, using ALE for microbolometer fabrication would allow the removal of excess mass, reducing the total heat capacity and improving sensitivity to absorbed radiation. Recently, an ALD microbolometer-type absorption structure was fabricated using an ALD on polyimide technique [1]. The structure consists of a thin ALD W layer surrounded by thin ALD Al₂O₃ layers, which can be thinned using ALE, if necessary. It should be noted that such a process is not limited to the development of microbolometer-type structures, but may be applied in any case where it is advantageous to remove redundant material post-release or from complex 3-dimensional structures. In the coming years more ALE chemistries will be explored for etching of diverse materials. Thermal ALE will no doubt permeate many micro- and nano-fabrication processes due to its self-limiting, conformal and atomically precise nature.

Figure 2. Ultra-thin ALD test structures [1], [11]. a) Microbridge with Al contact pads for thermal time constant measurements pre- and post-ALE. b) Microbolometer-type absorption structure made up of $\text{Al}_2\text{O}_3/\text{W}/\text{Al}_2\text{O}_3$ as fabricated pre-ALE.

FABRICATION

The fabrication of suspended microbridge test structures (Figure 2a) for ALE demonstration followed a similar process as outlined by Eigenfeld *et al.* [1]. A sacrificial polyimide layer was spun onto a bare silicon wafer to a thickness of $\sim 3 \mu\text{m}$ and cured. Next, ALD layers were deposited using a Beneq TFS 200 ALD reactor. The layers were deposited at 300°C in a trilayer configuration consisting of $6.15 \text{ nm Al}_2\text{O}_3/ 3.7 \text{ nm Ru}/ 6.15 \text{ nm Al}_2\text{O}_3$. The Al_2O_3 was deposited using TMA and H_2O precursors for growth at $\sim 0.13 \text{ nm/cycle}$. The Ru was deposited using thermally activated $\text{Ru}(\text{EtCp})_2$ at 110°C and O_2 for growth at $\sim 0.04 \text{ nm/cycle}$. The ALD layers were then patterned using a positive photoresist mask and a CF_4/O_2 reactive ion etch chemistry. Next, using a negative photoresist lift off process, Al was evaporated to form contact pads at the anchors of the microbridges. Finally, an O_2 plasma ashing process was used to remove the sacrificial polyimide layer and release the microbridges. The microbridges are on the order of $20 - 120 \mu\text{m}$ in length and $2 - 4 \mu\text{m}$ in width.

Microbolometer-type absorption structures (Figure 2b) were fabricated in a similar process as described above with the absence of Al contact pads. The layers were produced in a custom ALD W reactor and consisted of a nominal $\text{Al}_2\text{O}_3/\text{W}/\text{Al}_2\text{O}_3$ trilayer, which produces flat suspended absorption structures as previously demonstrated by Eigenfeld *et al.* [1]. The Al_2O_3 deposition was performed at 130°C for growth at $\sim 0.13 \text{ nm/cycle}$. The W deposition was performed at 130°C for growth at $\sim 0.38 \text{ nm/cycle}$.

Figure 3. X-ray reflectivity (XRR) data for thermal ALE of Al_2O_3 using $\text{Sn}(\text{acac})_2/\text{HF}$ and TMA/HF chemistries. Differences in the periodicity for pre- and post-ALE correspond to varied X-ray interference due to changes in the film thickness. a) The $\text{Sn}(\text{acac})_2/\text{HF}$ chemistry corresponded to $\sim 0.022 \text{ nm/cycle}$ etch rate. b) The TMA/HF chemistry at 300°C corresponded to $\sim 0.055 - 0.065 \text{ nm/cycle}$ etch rate depending on placement in chamber.

METHODS

Two thermal ALE chemistries have been found to etch Al_2O_3 using a fluorination and ligand exchange mechanism. As demonstrated by Lee *et al.*, $\text{Sn}(\text{acac})_2/\text{HF}$ and TMA/HF etch Al_2O_3 in a self-limiting process [2], [3]. Figure 3 demonstrates X-ray reflectivity data from Al_2O_3 coated Si test wafers confirming etch rates reported from Lee *et al.* for each chemistry in a custom built ALD/ALE reactor. Etching using $\text{Sn}(\text{acac})_2/\text{HF}$ was performed at 200°C with an etch rate of 0.022 nm/cycle . Etching using TMA/HF was performed at 300°C with an etch rate of $0.055 - 0.065 \text{ nm/cycle}$ depending on wafer placement in the chamber. Special attention was paid to precursor dose pressure and purge times to ensure surface saturation and self-limited behavior. Etch rates are subject to change with varied reactor parameters. For example, the $\text{Sn}(\text{acac})_2/\text{HF}$ etch rate was increased to 0.046 nm/cycle by varying dose pressures.

Mircopulse calorimetry was used to measure material removal on suspended microbridge test structures. This method was previously used to measure the specific heat capacity of ALD W, as outlined by Eigenfeld *et al.* [12]. The thermal time constants, τ 's, of the microbridge test structures are measured before and after ALE sessions. A pulsed step voltage is applied across the bridge (with a rise time $< 1 \mu\text{s}$) and a transient current response is monitored, which is several orders of magnitude slower than the voltage rise. This effect is a result of the temperature sensitive resistance responding to joule heating of the Ru and surrounding Al_2O_3 layers. An exponential decay function may be fit to the measured current response to extract τ for a given microbridge length. The experimental τ data can then be fit to extract the thermal diffusivity, α , where τ is given as,

$$\tau = \alpha l^2 / \pi^2, \quad (2)$$

where l is the microbridge length and α is given as,

$$\alpha = \kappa / \rho c_p, \quad (3)$$

where κ is the thermal conductivity, ρ is the density and c_p is the specific heat capacity of the microbridge [12]. To compare the measured time constant data to calculations using the expected thickness removal during ALE processing, κ and ρ of the microbridges pre- and post-ALE were measured following the methods outlined by Eigenfeld *et al.* [11]. The microbridges were joule-heated using a steady-state biasing technique and κ extracted using a temperature dependent resistance joule heating model. The

Figure 4. ALE reduces the thermal time constants of microbridges by material removal. After 140 cycles of ALE, about half of the total Al_2O_3 thickness was removed. After 280 cycles of ALE, all of the Al_2O_3 thickness was removed leaving just Ru. Curve fits correspond to the extraction of thermal diffusivity.

thicknesses and densities of the pre-ALE ALD films were also measured using X-ray reflectometry (XRR) on a Bede D1 X-ray diffractometer. The X-ray wavelength for measurements was 1.54 Å, corresponding to the $K\alpha$ transition in the Cu X-ray tube. The Bede REFS software was used to fit the XRR data and extract the thickness and densities of the ALD Al_2O_3 and Ru films. Using the measured κ and ρ and bulk c_p values, the measured thermal diffusivity, α_{exp} , may be compared with the calculated thermal diffusivity, α_{calc} , based on a relative thicknesses of Ru and Al_2O_3 contributions given as,

$$\alpha_{\text{calc}} = \frac{\alpha_{\text{Ru}} t_{\text{Ru}} + \alpha_{\text{Al}_2\text{O}_3} t_{\text{Al}_2\text{O}_3}}{t_{\text{Ru}} + t_{\text{Al}_2\text{O}_3}}, \quad (4)$$

where t is the thickness of the Ru or Al_2O_3 layers.

RESULTS

The τ 's of several lengths of the $\text{Al}_2\text{O}_3/\text{Ru}/\text{Al}_2\text{O}_3$ test structures were measured pre-ALE and then etched using the $\text{Sn}(\text{acac})_2/\text{HF}$ chemistry. Figure 4 demonstrates pre and post ALE etching with $\text{Sn}(\text{acac})_2/\text{HF}$. After each ALE session, the thermal time constants of the microbridges are reduced as Al_2O_3 is removed in increments of 140 and 280 $\text{Sn}(\text{acac})_2/\text{HF}$ cycles (Figure 4). Using equation 2, α was extracted (Figure 4 fit lines) for pre- and post-ALE sessions. Using measured κ , ρ , and bulk specific heat capacity, α_{calc} for the first 140 ALE cycles (red data Figure 4) using an expected 3.1 nm top and bottom Al_2O_3 etch falls within 13% of α_{exp} . For 280 ALE cycles, α_{calc} does not agree well with α_{exp} , likely due to complete removal of the Al_2O_3 and oxidation of the bare Ru structure upon transfer from the ALE vacuum system to the electrical probing vacuum system. Sources of error include slight variations in etch rates between the top and underside Al_2O_3 surfaces or the global etch rate due to reactor parameters. It is possible longer precursor exposure would reduce such error to ensure complete underside surface saturation for each ALE cycle. A notable increase in resistance of the Ru microbridges was observed after being exposed to atmosphere for several days.

Figure 5. Thermal ALE trials on microbolometer-type absorption structures with $\text{Sn}(\text{acac})_2/\text{HF}$ chemistry (b) and TMA/HF chemistry (d). (Figure 2b corresponds to a structure with heating and no ALE.) a) A control for the $\text{Sn}(\text{acac})_2/\text{HF}$ ALE process. No ALE with 16 hours at 200 °C. b) 67 cycles of $\text{Sn}(\text{acac})_2/\text{HF}$ at 0.046 nm/cycles. c) A control for the TMA/HF process. No ALE, but 16 hours at 300 °C. d) 51 cycles of TMA/HF. All structures are $16 \times 16 \mu\text{m}^2$.

The microbolometer-type absorption structures were subject to both etch chemistries to remove ~ 3.1 nm of Al_2O_3 on top and bottom of the structure. The $\text{Sn}(\text{acac})_2/\text{HF}$ chemistry was repeated for 67 cycles at the elevated etch rate of 0.046 nm/cycle and the TMA/HF chemistry repeated for 51 cycles at the typical etch rate. Additionally, the suspended structures were subjected to the etch duration and the given etch temperature with no ALE processing to determine if they would survive at elevated temperature for the etch duration and remain flat (Figure 5). The structures remained flat after being subject to both 200 °C and 300 °C for 16 hours with no ALE processing. After 67 cycles of ALE processing with $\text{Sn}(\text{acac})_2/\text{HF}$, the structure yielded negligible curling. After 51 cycles of ALE processing with TMA/HF, also yielded negligible curling.

To confirm the exposed metal sidewalls of the microbridge test structures and microbolometer-type suspended structures were not etched during the above experiments, each etching chemistry was tested for selectivity to Al_2O_3 in the presence of Ru and W. The top Al_2O_3 layer in a trilayer of ALD $\text{Al}_2\text{O}_3/\text{Ru}/\text{Al}_2\text{O}_3$ on Si was etched using $\text{Sn}(\text{acac})_2/\text{HF}$ at 200 °C and the top Al_2O_3 layer in a trilayer of ALD $\text{Al}_2\text{O}_3/\text{W}/\text{Al}_2\text{O}_3$ on Si was etched using $\text{Sn}(\text{acac})_2/\text{HF}$ at 200 °C and TMA/HF at 300 °C. For each etch, Al_2O_3 was removed completely, with a 10% overetch based on its thickness and ALE etch rate. The trilayer thicknesses and densities were measured using XRR pre- and post-ALE to determine if the Ru and W films were affected by the ALE chemistries during etch exposure. Figure 6 demonstrates the results of the selectivity etch experiment for $\text{Al}_2\text{O}_3/\text{W}/\text{Al}_2\text{O}_3$ using TMA/HF. After etching the top Al_2O_3 layer, a thin native metal oxide layer in the form of WO_3 or RuO_2 was formed after exposure to atmosphere during XRR on the order of a few nanometers. Using thickness and density calculations for oxide growth, the measured metal oxide thicknesses via XRR correspond to the expected oxide growth for an un-etched metal film. Figure 6 demonstrates this result for TMA/HF at 300 °C in the presence of Al_2O_3 and W. Similar results

Figure 6. ALE selectivity results for TMA/HF for Al_2O_3 and W. XRR results (below) show the top layer of Al_2O_3 was completely etched after a 10% overetch and an expected layer of native WO_3 formed.

were achieved for $\text{Sn}(\text{acac})_2/\text{HF}$ at 200 °C in the presence of $\text{Al}_2\text{O}_3/\text{W}$ and $\text{Al}_2\text{O}_3/\text{Ru}$. Further experiments for Al_2O_3 etch selectivity are underway for other materials.

CONCLUSION

The first ever demonstration of thermal ALE on suspended NEMS structures was demonstrated using $\text{Sn}(\text{acac})_2/\text{HF}$ and TMA/HF chemistries. Etching Al_2O_3 conformally on the top and underside of microbridge test structures was confirmed using micropulse calorimetry. Etching of microbolometer-type absorption structures to reduce thermal mass and maintain a flat suspended structure was achieved using TMA/HF. The $\text{Sn}(\text{acac})_2/\text{HF}$ and TMA/HF chemistries were selective to Al_2O_3 in the presence of ALD W and ALD Ru. The concept of conformal isotropic etching of suspended NEMS structure may be applied to a variety of niche fabrication processes for future devices. Further, ALE of a diverse subset of materials will open unique avenues for micro- and nano-device fabrication.

ACKNOWLEDGEMENTS

This material is based upon work supported by, or in part by, the U. S. Army Research Laboratory and the U. S. Army Research Office under contract/grant number W911NF-14-C-007. It is also supported by DRS Technologies Inc. and DARPA (Award #W911NF-14-C-007). N.T.E. performed the test structure fabrication, micropulse calorimetry experiments and analysis. J.C.G. performed custom ALE etching and XRR data analysis. G.D.S. and DRS technologies performed microbolometer-type structure fabrication. S.M.G. and V.M.B. offered expertise regarding ALE processes and ALE/ALD for N/MEMS. Fabrication was performed at the Colorado Nanofabrication Laboratory (CNL) and imaging at the Nano Characterization Facility (NCF).

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