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RASIRC
Lorenzo Diaz | Product Manager
Phone: 858-259-1220
E-mail: ldiaz@rasirc.com

Recent Progress on Low-Temperature Thermal Atomic Layer Deposition of Silicon Nitride Thin Films Using Anhydrous Hydrazine as Novel Nitrogen Source

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Owing to their unique optical, thermal, chemical, and electrical properties, silicon nitride (SiN) thin films are widely employed in semiconductor devices. As the technological node approaches the sub-1-nm, it necessitates the adoption of complex 3-D device architectures, further imposing stringent requirements on metal nitride thin film deposition processes. This highlights the advantages of the atomic layer deposition (ALD) process for metal nitride deposition over conventional deposition techniques like physical vapor deposition (PVD) and chemical vapor deposition (CVD).[1] ALD enables the fabrication of highly uniform, conformal films on both planar and intricate device structures while offering precise control over material thickness and composition. Moreover, ALD is particularly beneficial in back-end-of-line (BEOL) integration, where stringent thermal budget constraints demand low-temperature processing (<400°C) to prevent degradation of underlying materials and device performance.[2,3]

Herein, recent progress in the low-temperature depositions of silicon nitride thin films using anhydrous hydrazine (BRUTE ® hydrazine; N_2H_4) as novel nitrogen sources are highlighted. Since N_2H_4 exhibits higher reactivity and is more thermodynamically favorable in reactions compared to conventional ammonia (NH_3), hydrazine can effectively lower the deposition temperature of metal nitride thin films.[4]

The study was conducted at the RASIRC Nitride Hub using a custom-built ALD chamber without a sample transfer load-lock. A detailed schematic of the tool is available elsewhere.[5] In this setup, the chamber's exhaust line is divided into two separate paths. One connects the chamber to a dry pump for the ALD process, and the other leads to a high-vacuum turbo pump used to evacuate the chamber before deposition. To control the pump paths, two manual gate valves are used to direct the flow. The chamber wall and the exhaust lines are maintained at 120°C, while the precursor delivery lines are kept at 90°C to prevent precursor condensation. After loading the substrate into the chamber and performing rough pumping, the base pressure is reduced to ~10^{-6} Torr using the turbo pump. This step helps remove the bulk of ambient moisture

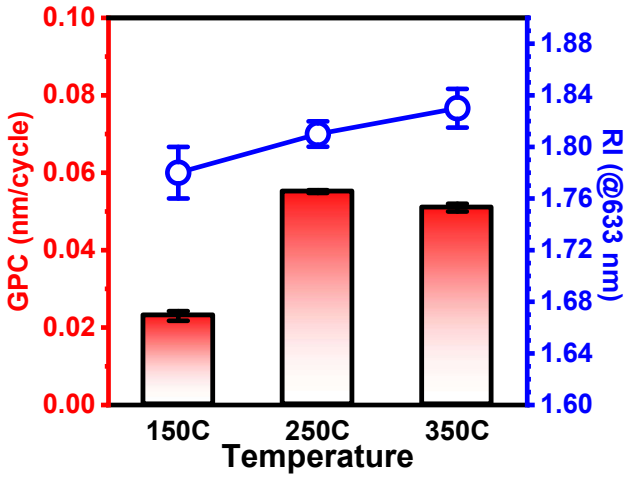

Fig. 1. *The GPC and RI values of N_2H_4-based ALD SiN thin films deposited between 150-350°C.*

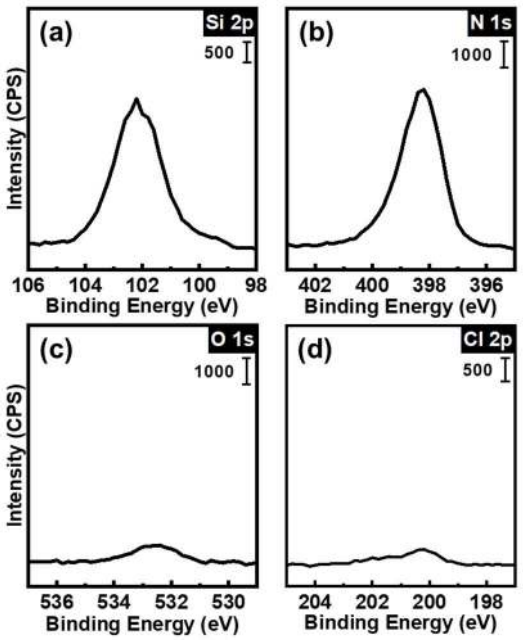

Fig. 2. *The high-resolution scans of (a) Si 2p, (b) N 1s, (c) O 1s, and (d) Cl 2p XPS regions of SiN thin film deposited at 250°C.*

introduced during sample loading, but some residual water is expected to remain in chamber. Once the temperature stabilizes at the set point for over an hour, the chamber is flushed with 75 sccm of N_2 for 20 minutes at a pressure of 0.5 Torr under rough pumping. One full ALD cycle of SiN deposition consists of a 1-second pulse of hexachlorodisilane (HCDS, Si_2Cl_6) followed by a 30-second N_2 purge, and a 0.3-second pulse of N_2H_4 followed by another 30-second N_2 purge.

As demonstrated in Fig. 1, the use of hydrazine effectively reduces the deposition temperature for ALD SiN to 150°C, achieving a growth per cycle (GPC) value of ~0.023 nm/cycle. As deposition temperature increased to 250°C or higher, the growth rate of the thin film doubled. The results indicate that, at temperatures below 250°C, insufficient thermal energy likely hinders surface reactions, resulting in a lower GPC. Between 150°C–350°C, the refractive index (RI), determined using ellipsometry at 633 nm, ranged from 1.78±0.01 to 1.83±0.01.

The composition of ~13 nm SiN deposited at 250°C was evaluated using X-ray photoelectron spectroscopy (XPS) (Fig. 2). The Si 2p peak, nearly symmetrical at a binding energy of ~102 eV, indicates Si–N bonding, while a strong N 1s peak at ~398 eV further confirms the successful deposition of SiN.[5] The low intensity of the O 1s and Cl 2p peaks suggest minimal oxygen and chlorine contamination, indicating a high-purity SiN thin film. The calculated O and Cl impurities embedded within the thin films were estimated to be 3±1 at. % and ~1±1 at. %, respectively. The observed oxygen content likely resulted from exposure to ambient air during the 30-minute sample transfer, while chlorine contamination may stem from insufficient thermal energy during deposition, leading to incomplete precursor reactions. The ratio of [Si]/[N] was approximately 1.05.

Overall, it is demonstrated that the use of anhydrous hydrazine as the novel nitrogen source effectively lowers the deposition temperature of SiN thin films to below 300°C, enabling high-quality film growth under reduced thermal conditions. Further optimization opportunities are available upon request.

About RASIRC and RASIRC Nitride Hub

RASIRC innovations convert low vapor-pressure liquid chemistries into safe and reliable gas flow for most processes. RASIRC technology delivers hydrazine gas and hydrogen peroxide gas in controlled, repeatable concentrations. RASIRC products include BRUTE® Peroxide, BRUTE Hydrazine, Peroxider® and RainMaker® Humidification System. These products incorporate proprietary and patented technology that enables them to deliver gas to process with precision. BRUTE® Hydrazine provides a stable, reliable flow of ultra-dry hydrazine gas from a liquid source in a sealed vaporizer.

RASIRC Nitride Hub is the industry's first dedicated program for rapid, side-by-side screening of metal nitride ALD precursors. This IP-secure environment supports faster material adoption by allowing direct comparisons of BRUTE® Hydrazine to traditional reactants such as thermal and plasma NH_3. The Nitride Hub removes a key barrier in semiconductor process innovation by enabling chemical manufacturers and end users to evaluate precursor compatibility with BRUTE® Hydrazine with minimal investment.

Reference

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P:858-259-1220, email ldiaz@rasirc.com or visit http://www.rasirc.com

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