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Improved ambient stability of thermally annealed zinc nitride thin films

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We report a remarkable improvement in the ambient stability of thermally annealed zinc nitride thin films. The scientific literature has yet to reach a consensus regarding some of the properties of zinc nitride (Zn$_3$N$_2$). While thermal annealing of Zn$_3$N$_2$ films under a flow of oxygen has been investigated as a method to thermally oxidize Zn$_3$N$_2$, thermal annealing to reduce ambient oxidation has not been investigated. We report that post-growth annealing significantly improves the stability of zinc nitride with a three-order magnitude increase in degradation time from a few days in un-annealed films to several years after annealing. A degradation study was performed on samples annealed under a flow of nitrogen at 200–400 °C, which showed that the stability of the films depends strongly on the annealing temperature. We propose a mechanism for this improvement, which involves a stabilization of the native oxide layer that forms on the surface of zinc nitride films after exposure to ambient conditions. The result holds significant promise for the use of zinc nitride in devices where operational stability is a critical factor in applications.
ensure stable sputtering conditions before opening the main shutter. Five samples from the same sputtering experiment (75 ± 2 nm) were annealed in a rapid thermal annealer for 60 s at temperatures between 200 °C and 400 °C under flowing nitrogen gas to investigate the effects of annealing temperature on the properties of the Zn$_3$N$_2$ films. Optical measurements (transmittance, reflectance, and spectroscopic ellipsometry) were performed within minutes of exposure of the films to an ambient atmosphere. The annealed samples were also characterized by spectroscopic ellipsometry, and all samples were monitored for several months to evaluate their stability. All optical measurements were performed on a J. A. Woollam Variable Angle Spectroscopic Ellipsometry (WVASE) ellipsometer, and the experimental data were modeled using the commercial WVASE software. The properties of the semiconductor layers were modeled using a Herzinger–Johs parameterized function.

A set of thicker samples (700 nm) was deposited and annealed with the same process to investigate the effects of annealing on the crystal structure of the Zn$_3$N$_2$ films by X-Ray Diffraction (XRD) measurements. All samples were stored in a cleanroom environment with regulated humidity and temperature levels for the duration of this study.

**RESULTS AND DISCUSSION**

It was initially observed that thermal annealing of Zn$_3$N$_2$ films under nitrogen improved their ambient stability, making the films less prone to oxidation. This is demonstrated in Figs. 1(a) and 1(b), which shows the optical transmittance of an as-deposited sample and a sample annealed at 300 °C, both monitored for a period of up to 18 weeks. The as-deposited Zn$_3$N$_2$ film was fully oxidized within 8 weeks, becoming transparent. In contrast, the annealed film showed no signs of oxidation over the full 18-week period. A cross-sectional SEM image of the annealed film after further exposure to ambient is shown in Fig. 1(c). The SEM image showed two clearly distinct layers: an oxide layer at the surface and a polycrystalline layer underneath it, followed by the amorphous substrate. Therefore, it was concluded that the annealed Zn$_3$N$_2$ film had been partially oxidized, although the oxide had been formed at a much slower rate.

To investigate the effect of annealing temperature on the rate of oxidation, a degradation study was performed on thin films (75 ± 2 nm) using spectroscopic ellipsometry measurements. Thinner films were selected for this study because they exhibited a very smooth surface. The details of the ellipsometric model that was used are discussed briefly in this section. Based on the observation in Fig. 1(c) of a multilayer structure produced through oxidation, we used a three-layer structure consisting of (a) the glass substrate, (b) the Zn$_3$N$_2$ layer, and (c) the oxide layer. The optical properties of the oxide layer were determined by fitting the model to the measurements of fully oxidized films. The properties of the Zn$_3$N$_2$ layers were determined by fitting the model to the measurements performed immediately after deposition and annealing. The refractive index and extinction coefficient obtained for the Zn$_3$N$_2$ layers are shown in Figs. 2(a) and 2(b), respectively. The obtained optical properties are in agreement with the expected values for both Zn$_3$N$_2$ [9,13,38] and ZnO/Zn(OH)$_2$ (not shown here; bandgap of ~3.4 eV, refractive index of 1.6–1.8). It is noted that the optical properties of the Zn$_3$N$_2$ layers shift with annealing temperature. Specifically, the absorption onset red shifts from ~1.4 eV to ~1.0 eV, and the refractive index decreases from 2.6 to 2.4. This trend indicates a change in the band structure of the material, which was attributed to changes in the structure of the films after annealing, discussed later in this paper.
The thicknesses of the Zn$_3$N$_2$ and oxide layers measured by ellipsometry are shown in Figs. 3(a) and 3(b) for up to 682 days after deposition. The as-deposited 75 nm film examined here was fully oxidized within 3 days of exposure to ambient. However, films annealed under nitrogen became increasingly more stable with increasing annealing temperature. At annealing temperatures of 350–400 °C, the films showed little or no signs of oxidation for up to 300 days after deposition. To explicitly illustrate the dramatic effect of annealing on stability, the time to full oxidation of the films was measured and is plotted as a function of annealing temperature in Fig. 3(c). The time to full oxidation increases from 3 to 1818 days for the as-deposited film and the sample annealed at 350 °C. The average rates of oxidation are listed in Table 1. The measured oxidation rate for the most durable samples is $10^{-1}$–$10^{-2}$ nm/day, which is several orders of magnitude lower than the as-deposited sample (order of 10 nm/day).

Further analysis of the data presented in Fig. 3(a) was performed to shed light on the underlying mechanism behind the improved stability. Two regions were identified in the oxidation process: an initial step with a slow oxidation rate (surface oxidation) and a subsequent step with an increased oxidation rate in the bulk of the films (bulk oxidation). The following mechanism is proposed to explain the observed results. Two reactions between Zn$_3$N$_2$, O$_2$, and H$_2$O species are commonly used in the literature to describe the process of oxidation,

\[
2\text{Zn}_3\text{N}_2 + 3\text{O}_2 \rightarrow 6\text{ZnO} + 2\text{N}_2, \quad (1)
\]

\[
\text{Zn}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Zn(OH)}_2 + 2\text{NH}_3. \quad (2)
\]

Following the initial formation of a native oxide on the Zn$_3$N$_2$ surface, reactions (1) and (2) indicate that further oxidation requires two steps: (a) the diffusion of O$_2$ and H$_2$O species through the oxide layer and onto the Zn$_3$N$_2$ surface, followed by (b) the reaction of the diffused species with the Zn$_3$N$_2$ surface, which results in the further growth of the oxide layer. Therefore, the improved stability with annealing temperature can be attributed to an improvement in the structural quality of the surface oxide layer, which makes it less permeable to O$_2$ and H$_2$O species. Over time, the newly formed oxide in step (b) likely damages the quality of the surface oxide and increases the average reaction rate. However, the diffusion of oxidizing species onto the Zn$_3$N$_2$ surface remains a rate-limiting step, as indicated by the very low oxidation rate throughout the entire oxidation process. The present study indicates that an annealing temperature of 350 °C is optimum for the observed improvement in stability, which suggests that the capping oxide layer begins to deteriorate at higher temperatures. Temperatures in the range of 400–600 °C are used in the literature to thermally oxidize Zn$_3$N$_2$ films.\textsuperscript{33,35,36} The (400) diffraction peak is shown in Fig. 4 for a set of samples annealed at 200 °C, 300 °C, and 400 °C. The graph shows that the (400) peak shifted to higher angles when annealed at high temperatures. This trend was

### Table 1. Time to full oxidation and oxidation rates for the annealed Zn$_3$N$_2$ films. Data indicated with an asterisk (*) were extrapolated based on available data.

| Annealing conditions | Surface oxidation duration (days) | Time to full oxidation (days) | Bulk oxidation rate (nm/day) |
|----------------------|----------------------------------|-----------------------------|-----------------------------|
| As deposited         | <1                               | 3                           | $3.5 \times 10^1$            |
| 200 °C               | 3                                | 18                          | $4.7 \times 10^0$            |
| 250 °C               | 13                               | 36                          | $3.0 \times 10^1$            |
| 300 °C               | 27                               | 257                         | $3.0 \times 10^{-1}$         |
| 350 °C               | 228                              | 1818$^*$                    | $4.4 \times 10^{-2}$         |
| 400 °C               | 228                              | 972$^*$                     | $9.4 \times 10^{-2}$         |

![Fig. 3. Thickness of (a) the Zn$_3$N$_2$ layer and (b) oxide layers over several months for annealed samples. (c) Lifetime of the Zn$_3$N$_2$ layer as a function of annealing temperature. The data points marked with * were extrapolated based on the oxidation rates measured in this study.](image-url)
The changes in strain observed for the $\text{Zn}_3\text{N}_2$ layer (up to several hundred nanometers). Post-annealing, the native oxide is stabilized and acts as a capping layer, significantly slowing down the oxidation rate. The dramatic improvement in the stability of $\text{Zn}_3\text{N}_2$ films demonstrated here provides a simple method to utilize the native oxide of $\text{Zn}_3\text{N}_2$ films without growing additional capping layers. This solves a major practical challenge in the research and development of $\text{Zn}_3\text{N}_2$, and technologies related to it.

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DATA AVAILABILITY

The data that support the findings of this study are openly available in the University of Sheffield data repository at https://doi.org/10.15131/shef.data.10049825 (see Ref. 44).

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