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# Ultra High Barrier Coatings by PECVD

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## Abstract

Silicon nitride barrier coatings are deposited using a large area, in-line PECVD source. The developed SiN films are dense and amorphous with a refractive index of 1.7-1.9 and no absorption in the visible (450-700nm). The films were deposited at <100°C making them suitable for low temperature substrates. A wet etch rate test was used to correlate barrier performance. The WER test is advantageous because it is independent of pinholes or defects and is relatively quick and inexpensive to perform. In this paper, WER results are correlated to SEM images of SiN films. Further useful information on the coating is gleaned by monitoring the WER for bubbles leaving the surface of the thin film.

### Introduction

Silicon nitride (SiN) is well known as a diffusion barrier coating, having been used as a semiconductor encapsulant for many years[i]. More recently SiN has been applied to polymer substrates to reduce permeation of water vapor and oxygen.[ii] One of the challenges when developing a thin film barrier process is determining the cause of poor results. Direct measurement of water vapor or oxygen transmission does not distinguish pinholes from coating porosity. This distinction is important in developing a barrier film. Using only the direct transmission method, a dense, amorphous film structure can be overlooked due to unrelated debris on the substrate.

We have found a buffered oxide etch (BOE) wet etch rate (WER) test is a good alternative barrier measurement technique. This test allows us to gain insight into the deposited film structure independent of particles or defects. Additionally, by monitoring the bubbles leaving the film during etching, nanometer scale features within the film can be detected.

Film morphology is critical to barrier performance. If the SiN thin film structure is dense and amorphous, the film is highly resistant to permeation by water vapor or oxygen. Barrier performance is greatly reduced for a porous film and/or a film with columnar structure. A second important requirement is good adhesion between the substrate and thin film. Our goal then is to make a uniformly dense, amorphous SiN film that is highly adherent to the substrate. And given the substrate is a polymer, to make this film at less than <100°C!

**Experimental**

Silicon nitride thin films are deposited by a large area PECVD process presented earlier[iii]. Of importance, the PECVD source has a self-cleaning attribute that keeps the electrode from coating up over time. Other benefits to the technology are uniform deposition over wide substrates, stable operation and high deposition rate. Figure 1 shows a view of this source for 1.25meter substrates

*Figure 1, AC Ion Source for 1.25m Substrate*

SiN films 1um thick were deposited on silicon wafers in a multi-pass process. The process goals were:

- Maximum substrate temperature: <100°C.
- Index of refraction range: 1.7-1.9
- Optically clear, no absorption in the visible range
- Maximum compressive stress: <100MPa

Using split lots, samples were dipped in the BOE solution and the WER measured. BOE solution used for all experiments was comprised of 6:1 volume ratio of 40% $NH_4F$ and 49% HF. This solution was designed to etch reference thermally grown $SiO_2$ at 100nm/min. Any bubbling from the film was recorded. Other samples were used to take SEM images.

**Results**

Initial development results showed the SiN films to have a columnar morphology (Figure 2). The WER of this film was rapid, 1um of SiN was etched within 15 seconds, and bubbling was witnessed over the entire etch period (Figure 3). The poor WER results correlated to the SEM image.

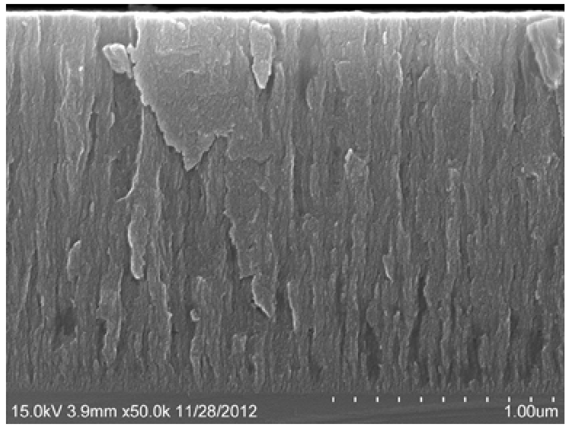


*Figure 2: Columnar SiN Structure*

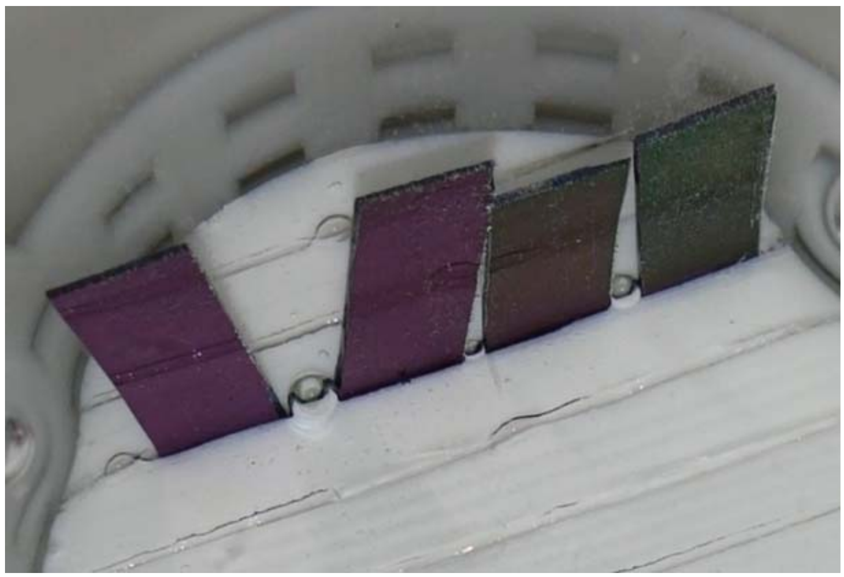

*Figure 3: Bubbling of thin film during WER test*

Continued development saw improvement in the layer quality; however, an interface between each coating pass remained visible (Figure 4). The WER for this film improved to 5 minutes. During etching, bubbles appeared on the film at regular intervals related to the number of coating passes. The SEM of the film confirmed a reduced density interface between each layer.

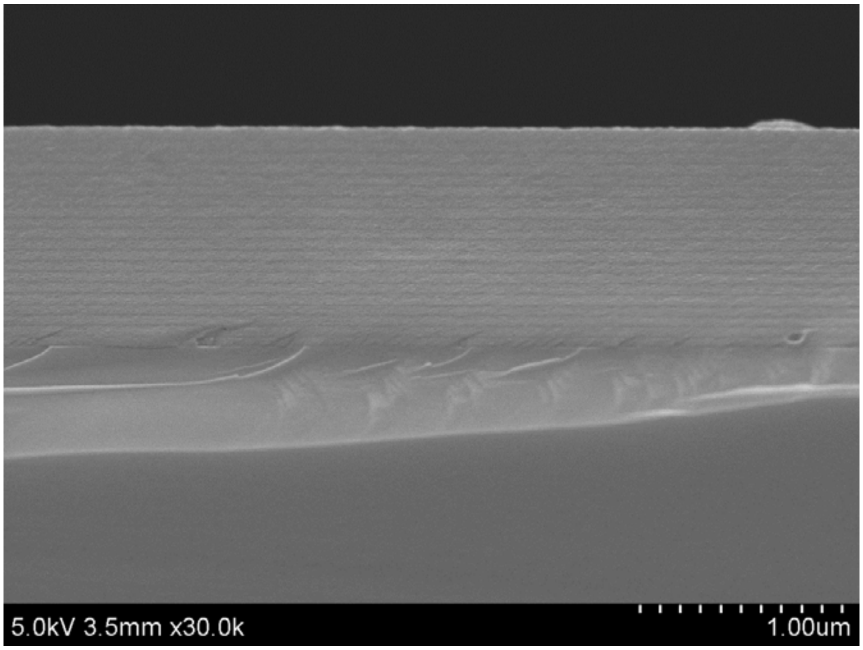


*Figure 4: Amorphous SiN with distinctive interlayer zones*

Further development led to achieving a dense, amorphous SiN film. Figure 5 shows an SEM image of this film. Note the lack of any visible interface between deposition passes. (This film was made using the same number of passes as the film in Figure 4.) In agreement with the SEM image, the WER improved to 19 minutes and no bubbling occurred at any time during etching.

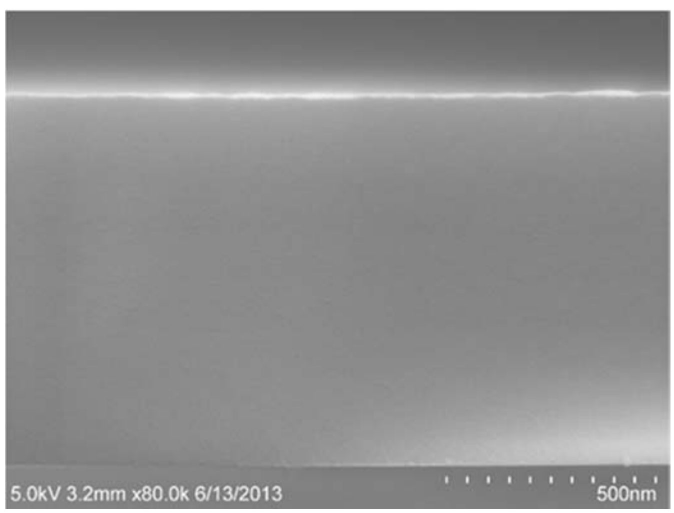


*Figure 5: Fully amorphous SiN with no visible interface zones between layers (same number of deposition passes as film in Figure 4)*

Adhesion testing was conducted per ASTM 3359, the standard grid and tape test. After coating, a grid pattern was cut into the thin film and adhesion was tested. Then the same sample with grid pattern was boiled in water for 10 minutes and adhesion was tested again. Finally, the sample is immersed in salt bath solution (100g NaCl in 600ml $H_2O$) at 80°C for 1 hour and adhesion then re-tested. Of all conditions, the adhesion was evaluated to be 5B. (This is the highest ranking for adhesion indicating the edges of all cuts are smooth and none of the lattice squares are detached.)

This film met all process goals: The substrate temperature remained below 100°C, they were optically clear with no color and the compressive stress was below 100MPa.

**Conclusion**

Dense amorphous SiN barrier coatings were deposited with a large area, in-line PECVD source. The films were deposited at <100°C, are optically clear (no absorption in the visible) and have low compressive stress.

The use of the BOE WER test was instrumental in the development of this film. The quick turn-around of the test allowed a wide process window to be investigated. Initially, samples were evaluated by both the WER test and SEM images. When the close correlation between WER results and film morphology was confirmed, fewer SEM images were required, accelerating the development program.

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[i] Pierson, Hugh O. (1992). *Handbook of chemical vapor deposition (CVD)*. William Andrew. p. 282

[ii] K. Akedo, A. Miura, H. Fujikawa, and Y. Taga, "Plasma-CVD SiNx / plasma-polymerized CNx:H multi-layer passivation films for organic light emitting diodes" in Proc. Soc. Inform. Display Symp., Dig. Tech. Papers, vol. 34, 2003, pp. 559-561

[iii] J Madocks, W Seaman, Society of Vacuum Coaters 54th Annual Technical Conference Proceedings (2011), 'Anti-Reflective Coatings by Plasma Enhanced Chemical Vapor Deposition on Large Area Substrates'