

# Etching and Characterization Studies of Ag/n-Si Nanocomposite Films

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## Abstract:

Studies were done on 3  $\mu\text{m}$  thick Ag/n-Si composite films prepared by magnetron co-sputtering. This material is being investigated for use as a photodetector for detecting radiation in the 8-14  $\mu\text{m}$  wavelength range. During sputtering, some Ag particles coalesce and create a segregated layer on the surface. In order to use the optoelectronically sensitive composite layer in a device, this segregated layer must be removed. Both an HF wet-etch and a  $\text{Cl}_2$  RIE dry-etch were employed. Resistivity measurements were taken to determine when, during the etching process, the segregated layer was removed; SEM imaging was used to confirm these conclusions. It was found that the wet etch altered the structure of the composite, while the dry etch left behind an involatile film of AgCl.

## Introduction:

The goal of this research is to design a material that will be incorporated into a device that will detect infrared radiation. This photodetector will absorb wavelengths of 8-14  $\mu\text{m}$ , which is a strong part of the blackbody emission for 300K. The material being studied contains Ag nano-sized particles uniformly distributed throughout a semiconductor matrix of n-Si. Photons in the 8-14  $\mu\text{m}$  wavelength range are absorbed by the Ag nano-sized particles. They produce photoexcited electrons that tunnel through the metal-semiconductor interface and give rise to a signal current in an external circuit.

Previous studies by this group have produced and characterized Ag/n-Si composites that absorb radiation in the desired range [1]. This has been achieved by co-sputtering 4:1 n-Si:Ag onto Si (111) substrates maintained at 400°C throughout deposition. At this sputtering temperature, the n-silicon remains amorphous within the composite. In order to achieve greater efficiency in our device, we want to sputter at a temperature high enough to crystallize the n-Si. However, higher sputtering temperature yields larger Ag particles and more dark current.

Although pure silicon crystallizes at 600-650°C, we prepared a fully crystalline matrix by sputtering at 550°C. This is due to metal-mediated crystallization, in which the silver particles act as crystallization sites for the n-Si [2]. We chose a sputtering ratio of 4:1 Si:Ag because at 20 at%

Ag there are enough Schottky junctions to proliferate a photocurrent while still minimizing dark current. This is because at 20 at% Ag, the composite is at half its percolation threshold, which is the point at which continuous paths of Ag are produced throughout the Si matrix.

Silver particles within the composite tend to rise to the surface and form a segregated layer. This phenomenon occurs because Ag particles achieve lower energy by avoiding contact with silicon. This segregating effect actually occurs at all deposition temperatures but increases with temperature. Sputtering at 400-550°C creates a layer of Ag particles equal in thickness to approximately 5-10% of the 3  $\mu\text{m}$  composite film. It is important to note that below this segregated layer, uniformly embedded Ag particles still remain throughout the Si matrix. The segregated layer must be etched away so we can incorporate this composite into a device.

## Procedure:

Cleaved 1  $\text{cm}^2$  portions of 550°C sputtered wafers were etched using a wet etch as well as a dry etch. The material was periodically removed from etching and the resistivity of the film was measured using a four-point probe. Etching was discontinued after the resistivity increased to resemble

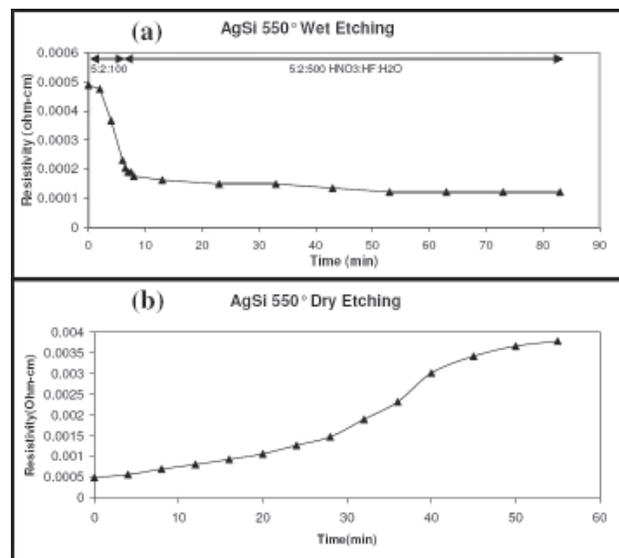


Figure 1. Resistivity vs. etching time: (a) wet etching, (b) dry etching.

that of our n-Si, which ranges from 0.005 to 0.011  $\Omega$ -cm. To confirm the removal of the segregated layer, the sample was cleaved, mounted perpendicularly, and cross-sectionally imaged with an SEM.

The wet etch technique first employed consisted of an etching solution of 2:5:100 HF:HNO<sub>3</sub>:H<sub>2</sub>O. The sample was submerged in solution and agitated with an ultrasonic bath at one minute intervals for 7 mins. The solution was then diluted to 2:5:500 and the sample was submerged for ten minute intervals for another 80 minutes.

The dry etch technique was a reactive ion etch of Cl<sub>2</sub>. We etched in 4-5 minute intervals for 55 minutes.

### Results and Conclusions:

In previous studies of composites sputtered at 400°, the chemical etch uniformly reduced the material without changing the structure of the composite layer. For the composites sputtered at 550°, however, this was not the case. Etching these samples only decreased the resistivity of the material from its initial value of  $5 \times 10^{-4}$   $\Omega$ -cm to more closely resemble the resistivity of metallic silver (Figure 1a). SEM cross-sectional images of the material before and after the etching process appear in Figures 2a and 2b, respectively. From these images, it is apparent that the etching process altered the physical structure of the composite. While the structure originally appears solid, it appears porous after etching. This analysis suggests that the chemical etch selectively etches silicon, leaving behind a composite of higher atomic % silver. These results were confirmed by Rutherford backscattering analysis of the etched films.

In contrast, the dry etch technique did not alter the structure of the composite. As shown in Figure 1b, the resistivity increased during the etching to closely resemble the value of the n-Si. This suggested that we were successful in exposing the composite. However, SEM imaging showed that the etching left an involatile product, AgCl, on the surface (Figure 2c).

In conclusion, we found that the differing properties of crystalline and amorphous Ag/n-Si composites greatly influenced our etching results. The same etch that left intact an amorphous matrix of silicon deformed the physical structure of a crystalline matrix.

### Future Work:

An efficient procedure for removing the segregated layer from these materials will be pursued further. Once this is completed, Hall measurements can assess the transport properties of the composite, and absorption data can test its optical properties.

### Acknowledgements:

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### References:

- [1] C.W. Bates, Jr., unpublished results.
- [2] T.J. Konno, R. Sinclair, *Phil. Mag.*, B71 (1995) 163.

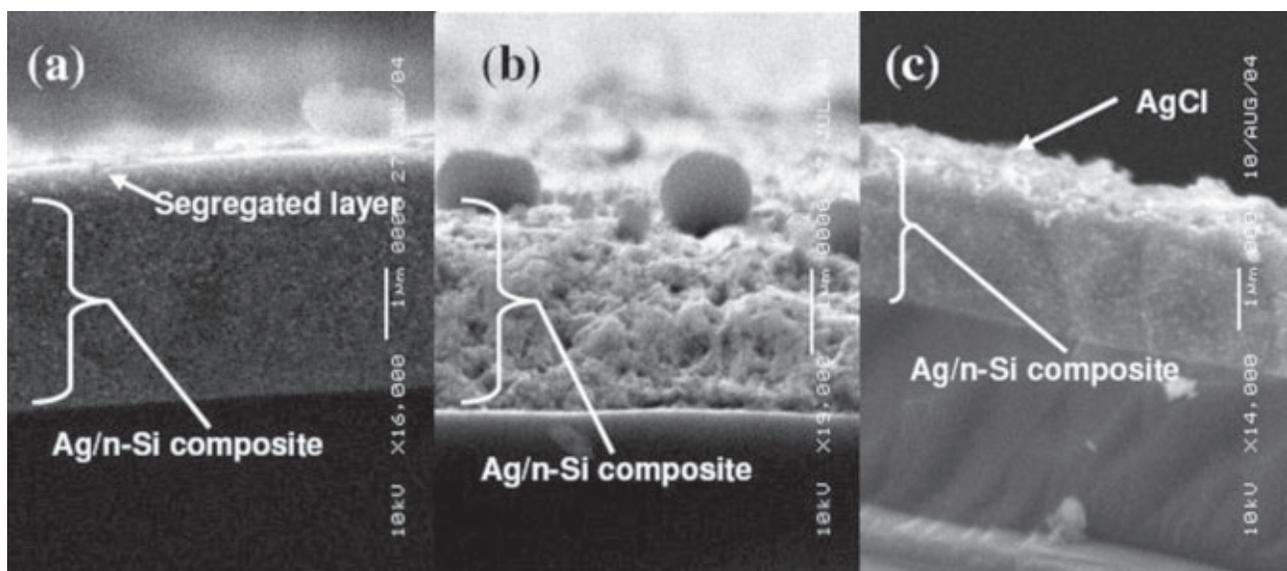


Figure 2: SEM cross-sectional: (a) before etching, (b) after wet-etch, (c) after dry-etch.