CHARACTERIZATION OF PECVD SILICON NITRIDE PASSIVATION WITH PHOTOLUMINESCENCE IMAGING

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ABSTRACT

In this paper, we present studies of plasma-enhanced chemical vapor deposited silicon nitride in which photoluminescence imaging was used to characterize our deposition process. A showcase of different processing issues such as equipment design, processing conditions, and manual handling is presented. We also demonstrate how photoluminescence imaging can be particularly useful for process monitoring, diagnoses, and development. An increase in implied V_{oc} of up to 25 mV was achieved through the use of PL imaging as a diagnostic tool.

INTRODUCTION

Photoluminesence (PL) imaging of silicon wafers [1,2] is a powerful technique to characterize surface passivation. It is fast and provides spatial information that is helpful in determining the nature of surface recombination processes. PL imaging is particularly powerful for developing silicon nitride as a passivation layer because, unlike thermal oxide films, silicon nitride films show a rich variety of spatially resolved effects, even in samples with exceptionally good quality passivation layers.

In this paper, we present initial studies of plasma-enhanced chemical vapor deposited (PECVD) silicon nitride (SiN) films in which PL imaging was used to characterize our SiN deposition process. We show how PL imaging can be used to understand the deposition process, key manual handling issues, thermal annealing processes, and the effect of post-deposition chemical processing. Given the rapid progress made at UNSW in the first three months of PL image analysis, it is clear to us that the technique will have an immediate impact on the development of better quality silicon nitride passivation films.

EXPERIMENTAL DETAILS

In this work, we use float zoned, 1 ohm.cm, <100>, n-type, silicon wafers. They were prepared by saw damage etching, RCA cleaning, and HF dipping prior to PECVD SiN deposition. The wafers were typically 240-microns thick.

SiN was deposited on both sides of the samples, one side at a time, using a Roth & Rau AK400 PECVD system at 400ºC and 0.2 mbar. The gas flow ratio of SiH_4 and NH_3 was varied to achieve a range of different refractive index films, and the deposition duration was varied to achieve optimum anti-reflection (AR) coating thickness for different SiN films.

The samples were characterised using the quasi-steady-state photoconductance (QSSPC) [3,4] and transient photoconductance (PCD) [5,6] lifetime testing techniques. The implied open circuited voltage (V_{oc}) [7,8] of the samples were extracted from the injection-level dependent lifetime data.

PL images were taken using an intense, infrared laser to illuminate the sample homogeneously with the equivalent of up to about two to three suns illumination intensity. The PL signal was recorded using a thermoelectrically cooled CCD camera. All images presented here were measured with PL detection from the illuminated front surface. The data acquisition time in all measurements presented here was one second.

Since the type of PL imaging that we used is for comparative, qualitative analysis, care was taken to control the illumination intensity between samples in different experiments. This was done by using a well-characterized control sample to standardize the experimental results. In this way, samples measured at different times can be compared more readily.

RESULTS

Figure 1 shows typical PL images of a diffused and thermally oxidized wafer and a SiN coated wafer. Lighter regions in the image correspond to a stronger PL signal and proportionally higher local excess carrier density. Since we use float zoned wafers and take care to avoid bulk contamination, light regions correspond to regions of low surface recombination and vice versa.

Except for the substrate holder marks in the SiN-passivation sample, both samples appear uniform to the naked eye. Notably, while the PL image of the diffused and oxide passivated sample is uniform in appearance, the PL image of the SiN-passivated sample is rich with details and features. This is even more remarkable considering that the one-sun implied V_{oc} of both samples

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were more than 700 mV. Clearly, even better passivation quality is possible if the regions of poor surface recombination appearing in Figure 1 can be understood and eliminated.

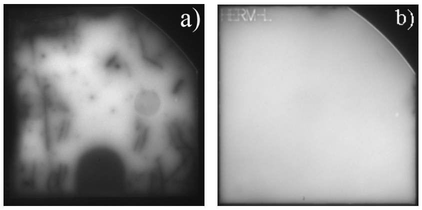

Figure 1: PL images of a typical (a) SiN coated and (b) diffused/oxidized silicon wafer. Both samples have implied open circuit voltages of >700 mV.

In this paper we will demonstrate how the PL imaging technique can be used as a tool for problem diagnosis and process development, using a broad spectrum of examples.

Impact of Equipment Design on Passivation Quality

One of the dominant features of the PL image shown in Figure 1a is the large dome-shaped dark region on the bottom side of the wafer. This region of poor surface passivation quality was found to be caused by the design of the substrate holder used in our PECVD deposition chamber. Importantly, the dome-shaped dark region (which is pointed out by the arrows in the images in Figure 4) extends well into the device active area, where it can affect the performance of our solar cells.

Figure 2 shows both the top view and side view of the graphite substrate holder that we use. The eight square indented areas across the substrate holder hold eight semi-square samples. Each square has two semi-circular indented areas to enable tweezers to scoop underneath the sample during unloading.

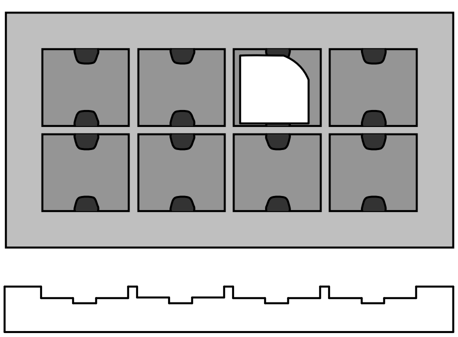

Figure 2: Top view and side view of the PECVD chamber substrate holder that is used at UNSW. The white semi-square shows a typical position of the sample in the substrate holder.

Closer examination of the PL images reveals that there are two substrate holder marks on every sample. Because the samples tend to slide to one side of the square indentation (as indicated by the position of the wafer in Figure 2), only one substrate holder mark prevails in the image. Furthermore, the marks in the PL images only appear on the sides that are face down during the first deposition, but not on sides that are face down during the second deposition. This was verified by turning the wafer 90^{o} for the second deposition and noting that the marks did not appear on the perpendicular edge. This suggests that the effect is caused by back sputtering of the graphite holder or the deposition of poor quality silicon nitride on the back during the first deposition.

The effect was minimized after careful redesign of the substrate holder. The passivation of the SiN films improved, and in some cases the implied V_{oc} increased by up to 25 mV. Figure 3b shows the PL image of a SiN film deposited in the improved substrate holder in same process conditions as the sample in Figure 3a. As shown in Figure 3b, the large dome-shaped dark region was eliminated.

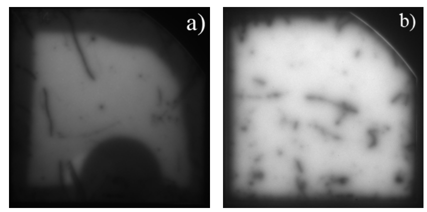

Figure 3: PL images of two samples: (a) deposited in the old substrate holder; (b) deposited in the improved substrate holder.

Impact of Processing Conditions

PL images suggest that the area affected by the substrate holder mark depends on the SiH_4/NH_3 gas flow ratio used during the deposition. Figure 4 shows three different samples with different SiH_4/NH_3 gas flow ratios. All samples were carefully oriented in the substrate holder such that the substrate holder mark would appear at the top and bottom edges of the samples.

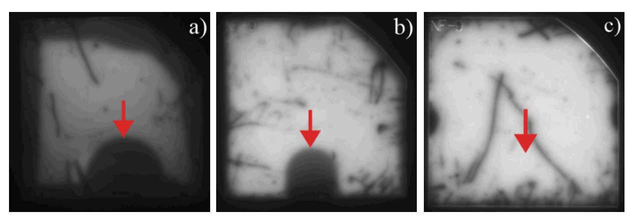

Figure 4: Samples with three different SiH_4/NH_3 ratios: a) 26:34 sccm; b) 31:29 sccm; c) 60:0 sccm. All images were taken in succession, ensuring that the optical generation rates were comparable between samples.

Visually, the substrate holder marks are roughly the same size for these three samples. The size of the affected area from the substrate holder in the PL images, however, shrinks with increased gas flow ratio. The sample with zero NH_3 (Figure 4c) appears to not be affected by the substrate holder, with no large dome-shaped dark region or dead areas around the edge. This suggests that the NH_3 plays an important role in the formation of the dark dome-shaped regions caused by the substrate holder; and/or the extra hydrogen incorporated in the cases of higher gas flow ratio plays an important role in passivating the poor quality region.

It should be noted the that smaller semi-circular marks on the left and right side of the sample in Figure 4c are caused by manual handling with tweezers during the RCA clean [9].

Impact of Manual Handling on Passivation Quality

PL imaging can also help identify how sample handling can affect the passivation quality of the SiN films. Figure 5 shows a few PL images that highlight handling related issues.

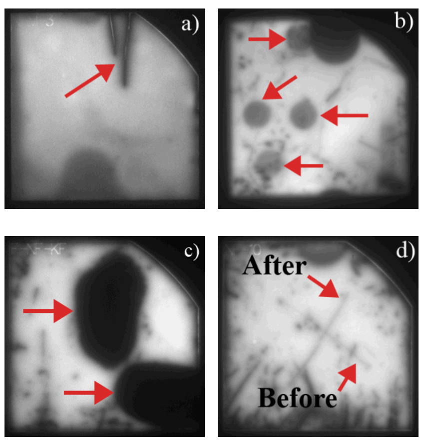

Figure 5: SiN samples showcasing poor sample handling: a) sample with micro-cracks; b) sample with micrometer marks; c) sample with finger prints; d) scratch test.

Figure 5a shows how PL imaging can detect micro-cracks that are not visible to the naked eye. The PL image in Figure 5b reveals that the micrometer used to measure the wafer thickness, either before or after the SiN deposition, can also lead to localized regions of high recombination. Note the four perfectly round dark circles in Figure 5b. These micrometer marks are not visible to the naked eyes. As indicated by the relative intensity of the PL signal, the passivation quality on the affected areas is about half of the unaffected area on the sample.

Figure 5c demonstrates that careless manual handling could make a huge impact on the passivation quality of nitride films. The two big oblong-shaped dark regions were caused by careless manual handling where fingerprints were visible on those two places on the sample. Visually the size of the actual fingerprints was about two-thirds of the affected area in the PL image. The passivation quality of the two affected dark regions is about 15 times worse than the unaffected area on the sample, as indicated by the relative intensity of the PL signal.

Figure 5d illustrates the impact of scratches on passivation quality. In this case, two very light scratches were deliberately made on the sample, one before and one after the SiN deposition. The image suggests that even very light scratches, both before and after deposition, can measurably reduce the local effective lifetime.

Process Monitoring with PL Imaging

At UNSW, the passivation quality of the samples in the same deposition run is occasionally inconsistent from sample to sample. Occasionally, a particularly bad sample may be found in a batch run. Since the PL imaging technique is fast (typically 1 second for the samples studied here), it is a powerful tool for process monitoring and control in cases like these.

Figure 6 shows two samples prepared identically in the same deposition run. One sample clearly has better passivation than the other, as indicated by comparing the PL intensity in the images.

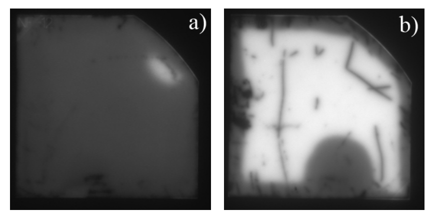

Figure 6: PL images of two samples prepared identically in the same batch and deposition run.

This observation from PL imaging also agrees with the QSSPC measurements, as the sample on the left hand side has an implied V_{oc} of 665 mV and the one on the right hand side has an implied Voc of 718 mV.

Impact of Annealing Conditions on Passivation Quality

Post-deposition annealing in moderation is known to increase the surface passivation quality of some SiN films. The poorly passivated sample shown in Figure 6a was subjected to annealing at 500°C for 5 minutes in N_2 ambient in a resistively heated, quartz tube furnace. QSSPC measurement indicated that the implied V_{oc} of this sample increased to 736 mV after annealing. Figure 7b shows the PL image of the sample after annealing.

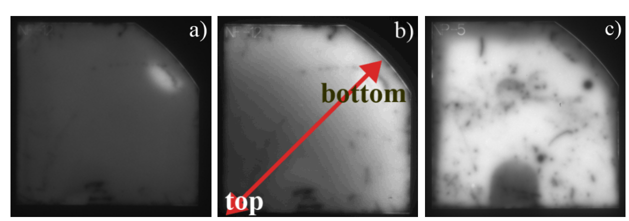

Figure 7: Photoluminescence images taken (a) before and (b) after annealing. (c) Samples annealed in a different furnace.

Apart from the time and temperature of annealing, PL images reveal that the annealing conditions also play an important role. As shown in Figure 7b, there is a gradient in the recombination rate across the sample after annealing. This is most likely due to a temperature gradient in the furnace used to perform the annealing. All other samples processed in the same annealing furnace showed the same gradient, whereas all samples processed in a different furnace show no gradient in the PL images, as shown in Figure 7c. Factors such as the type of boat used, loading and unloading rate, and gas flow inside the furnace could contribute to such gradient.

Impact of Post-deposition Wet Chemical Processing

In solar cell processing, SiN films are sometimes subject to various processes after the deposition, for example, wet processes that contain chemicals such as hydrofluoric acid (HF) or sodium hydroxide (NaOH).

Figure 8 shows the PL images of a sample with SiN films on both sides before and after undergoing a weak HF etch. As illustrated in the PL images, the overall passivation quality decreases after the HF etch, indicated by duller image (and hence a lower detected intensity). The overall intensity of the PL signal dropped by about 20%, and the implied V_{oc} dropped by about 10 mV, as indicated by the QSSPC measurements. Visually, the appearance of the sample became patchy after etching, corresponding to the patchy regions seen in the PL image in Figure 8b.

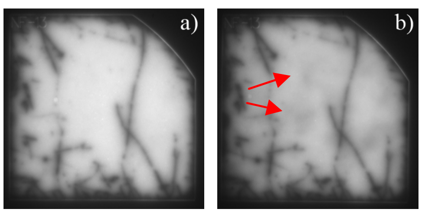

Figure 8: PL images of a sample taken (a) before and (b) after a weak HF etch.

Figure 9 shows another sample subjected to a NaOH etch process. Again, the overall passivation decreases, with an overall PL intensity drop of 25% and implied V_{oc} drop of 15 mV. Visually, the sample showed an increase in etched out pinholes in regions corresponding to the many tiny dark spots in PL images.

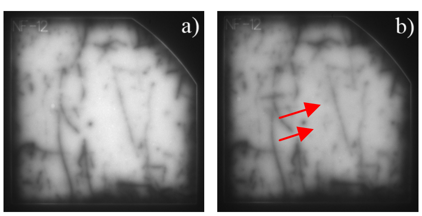

Figure 9: Before and after undergoing NaOH wet chemical process.

It is unclear whether the patchy regions and tiny dark spots in the PL images are due to local reduction of effective lifetime, or the change in optical properties that can affect the PL signal. Further investigation is needed.

CONCLUSION

PL imaging is a powerful tool for the characterization of silicon nitride passivation films. Here, we have highlighted some of the important applications, ranging from handling to process design that benefit from PL image analysis. Since it is fast and provides valuable spatial clues, it is an effective tool for identifying and rectifying problems. Importantly, all of the samples presented here exhibit excellent surface passivation quality, as measured with standard QSSPC and PCD techniques. By combining PC measurements with PL imaging, which provides valuable spatial information, improvements to the surface passivation quality is achieved.

ACKNOWLEDGEMENT

This work was produced with the financial assistance of the Australian Research Council under the ARC Centres of Excellence Scheme. The authors would like to thank Kate Fisher and Brett Hallam for their assistance in sample preparation.

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