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Silicon Surface and Heterojunction Interface Passivation Studies by Lifetime Measurement

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ABSTRACT

We report two investigations conducted by using photoconductivity decay lifetime measurement. The first is crystalline silicon (c-Si) surface passivation using quinhydrone/methanol (QM) for bulk minority-carrier lifetime measurement. QM shows great promise as a substitute for iodine-based solutions because of its superior stability and minimized surface recombination velocity in silicon. The second is interface passivation in an amorphous silicon (a-Si)/c-Si heterojunction structure as a parallel effort to develop and optimize heterojunction c-Si solar cells by hot-wire chemical vapor deposition (HWCVD). A thin buffer layer inserted between the a-Si and the c-Si substrate has been found to be much more effective than a directly deposited a-Si/c-Si interface in reducing the interface recombination velocity.

INTRODUCTION

In photoconductivity decay measurements, surface passivation is essential to obtain an effective lifetime that is close to the bulk minority-carrier lifetime in a silicon wafer, so that the true photovoltaic performance potential may be assessed. Various methods have been developed over the years to passivate silicon surfaces for this purpose. The most convenient and commonly practiced technique is iodine in methanol/ethanol solutions. However, quinhydrone/methanol seems to be even more stable and effective [1]. We report our experiments here confirming these claims and, hence, QM is used in our lifetime measurement procedure for wafer screening and other experiments.

When making a heterojunction with an intrinsic thin layer (HIT®) solar cell [2], a well-passivated c-Si/a-Si interface is very crucial for minimizing junction recombination and, therefore, to achieving a high-performance photovoltaic device. A real heterojunction is also very important for attaining a high open-circuit voltage [3]. That means a truly amorphous silicon layer must be deposited immediately on a c-Si surface. A buffer layer is therefore needed to help passivate the interface as well as to facilitate amorphous silicon deposition. Lifetime measurement offers a quick and accurate evaluation of the effectiveness of the buffer layers in passivation before completion of device-fabrication steps. This study attempts to quantify the passivation effects of a single-sided buffer layer deposited in a wedge form of materials ranging from no film to thick films.

EXPERIMENTAL

To carry out this study, we cut 6.35-cm x 6.35-cm squares or 1-cm x 2-cm

rectangles from 100-mm CZ-Si wafers with (100), p-type (B-doped), 11 Ω·cm, single-side polished, and damage-removal etched back surface. These samples are then subjected to a stringent cleaning procedure. They are degreased with trichloroethylene, acetone, isopropyl alcohol, and methanol and dried with nitrogen. This is followed by an immediate 10-min soak in boiling de-ionized (DI) water (90 MΩ·cm), 1-min DI water cascade rinse, 1% by volume hydrofluoric acid (HF) dip for 1-min or until hydrophobic, 1-min DI water cascade rinse, and drying with nitrogen.

The cleaned samples are either immersed in a nearly saturated quinhydrone/ methanol solution for lifetime measurements, or undergo a buffer layer/a-Si deposition process on the polished face of the wafers and are measured for lifetime. Buffer layer and a-Si depositions are all done in a HWCVD system.

Lifetime measurements were performed with a system and method developed at NREL [4] that uses the radio frequency photoconductivity decay (RF-PCD) technique operating in the ultrahigh frequency (UHF) range of 700 MHz. Our minority-carrier injection source was an attenuated 1064-nm YAG laser with a spot size of approximately 5 mm. This allowed us to make lifetime profiles across the graded a-Si and buffer layer wedges. Injection levels were not measured, but great care was taken to keep conditions consistent and injection levels as low as possible.

QUINHYDRONE/METHANOL SURFACE PASSIVATION

From the findings of H. Takato et. al. [1], a mixture of 0.01 to 0.05 mol/dm^3 of QM yields a solution capable of surface passivation superior to iodine and methanol (IM) or ethanol solutions. The principle benefits of the QM solution are a stable surface passivation that is reached after a development period dependent upon quinhydrone dilution anywhere from 10-min to several hours. Surface recombination velocities as low as 4.2 cm/s for 150-Ω·cm, p-type, (100), FZ-Si and stabilities that are measured on an hour timescale were reported [1]. The IM solutions achieve similar surface recombination velocities but have very poor stability with failing effectiveness immediately after submersion. Our own experiments with nearly saturated solutions of quinhydrone in methanol showed similar effects as in [1], with solution response after an initial 10-min development time. Fig. 1 illustrates the lifetime for three different surface conditions for 1-cm x 2-cm samples cut from the same 100-mm wafer: an as-received wafer without any surface passivation or cleaning steps, as-cleaned samples with 1% HF dip hydrogen-terminated surface, and QM-solution-passivated samples measured over time up to 60-min. The as-received surface is very poorly passivated with an effective lifetime of about 6 μs. After the cleaning procedure, the lifetime more than doubled owing to a hydrogen-terminated surface with variations from sample to sample of between 15.7 to 21.6 μs. For QM-solution passivation, lifetime increased by more than an order of magnitude after development time of 10-min from an initial value of 16.7 μs to a final value of around 90 μs. The nearly saturated QM solution we used stabilized much quicker than the 1 hour reported by Takato et. al. for 0.05 mol/dm^3 and appears to exhibit similar stability.

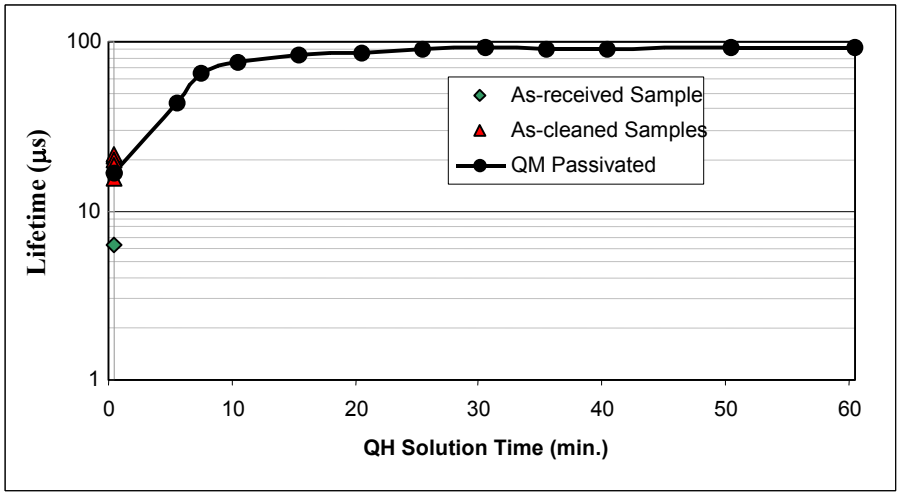

Fig. 1. Plot of as measured lifetime using RF-PCD technique for as-received, as-cleaned, and quinhydrone/methanol-solution-passivated samples.

HETEROJUNCTION INTERFACE PASSIVATION

We have deposited thin films of intrinsic a-Si on crystalline silicon substrates with different buffer layers using our own in-house HWCVD systems capable of depositing 5-cm x 5-cm combinatorial films on 6.35-cm x 6.35-cm substrates [3]. The advantages of this technique are no plasma damage to the surface, no plasma instability, high deposition rate, in-situ atomic hydrogen treatment, and a simplified deposition system. Because of system limitations, films and surface treatments were performed on a single side of the c-Si substrate. This poses a problem for accurate minority-carrier lifetime measurement because there is still a significant amount of surface recombination at the back surface. On a relative scale, the results of lifetime measurements on single-side passivated silicon substrates are still valid, nevertheless.

From the results of Fig. 2, buffer layer A (BL-A) by itself contributes very little to surface passivation based on the minimal change in measured lifetime. Minor lifetime improvement was observed for intrinsic amorphous silicon deposited on c-Si and for buffer layer B (BL-B) on c-Si. The a-Si was deposited at 200°C substrate temperature for 1-min with tungsten filament temperature of 2000°C. The largest improvement in surface passivation as indicated by the magnitude of rise in lifetime from 7 to 16 µs was the i-a-Si/BL-A layers deposited on c-Si. The sharp rise and fall in lifetime at the ends are an indication of the edge of the deposited film, and lifetimes at the edge correlate well with the other samples' endpoints. Fig. 3 shows lifetime values on a combinatorial deposition of graded i-a-Si from 0 to 60 nm in thickness vertically with an increasing thickness of BL-A horizontally. The thinnest layer depositions are in the upper left-hand corner and the edges with lifetimes of 6 µs, indicating the edge of the combinatorial mask and revealing some misalignment to the substrate and the scanning shutter. The measured lifetime as one moves down vertically near the left edge increases steadily in value. If one scans to the right from the upper left corner, the lifetime does not change appreciably

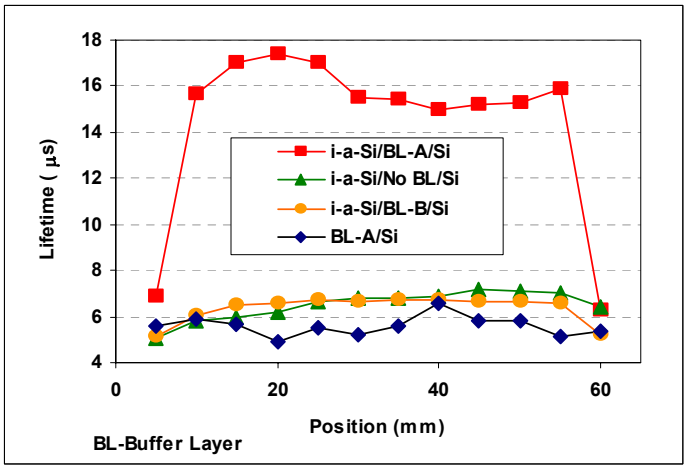

Fig. 2. Lifetime as a function of position (corresponding to increasing i-a-Si thickness if applicable) of different i-a-Si and buffer layer A/B combinations.

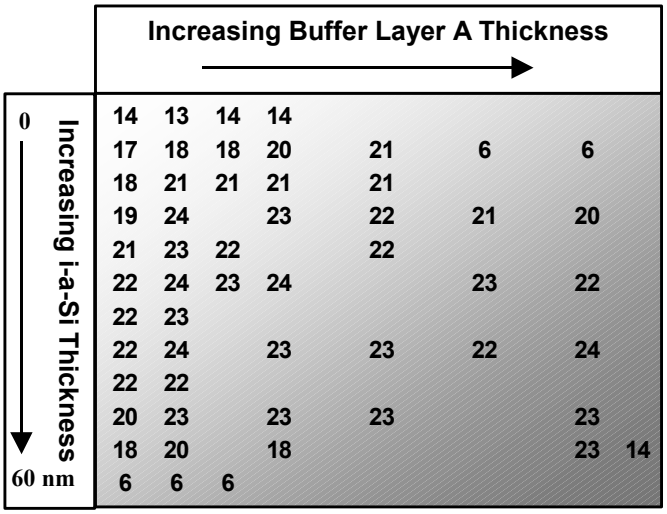

Fig. 3. Lifetime map in microseconds of combinatorial deposition of i-a-Si and BL-A layer wedges on a c-Si substrate.

for constant thin i-a-Si film, indicating that BL-A deposition alone is not adequate to passivate the interface, which correlates well with Fig. 2. However, at one-third of BL-A's maximum thickness, only about 10 nm of i-a-Si is sufficient to passivate the interface well, compared to nearly 30 nm of i-a-Si when BL-A is almost absent. BL-A's significance in assisting i-a-Si for effective interface passivation leads us to speculate that it immediately forces the deposition of a-Si rather than the usually poor epitaxial silicon, as confirmed by high-resolution TEM studies. Fig. 4 shows the lifetime variations on the same piece of sample along the i-a-Si thickness wedge deposited over BL-A and buffer layer C (BL-C) where BL-C is a co-deposition of BL-A and BL-B. The co-deposition material reveals further enhancement in lifetime, which may be attributed only to improved interface passivation because other variables are exactly the same between BL-A and BL-C. The behavior of the lifetime with i-a-Si thickness in Fig. 4 is similar to Fig. 3, except that the bulk lifetime of this particular sample was not as high, which resulted in lower measured lifetime. Again, we see that 10 nm of i-a-Si is enough for effective passivation when a good buffer layer is inserted.

CONCLUSIONS

The results of this study confirm that quinhydrone/methanol chemical solution is very effective and practical for silicon surface passivation for accurate bulk minority-carrier lifetime measurements. Compared to prior reports, the nearly saturated quinhydrone/methanol solution showed a shorter development time of only about 10-min to reach maximum surface passivation and demonstrated excellent stability.

Heterojunction interfaces of intrinsic amorphous silicon on c-Si showed significantly improved passivation with the use of a buffer layer. In particular, our BL-C buffer layer was the most effective in enhancing intrinsic amorphous silicon thin layer passivation of the crystalline silicon interface, potentially leading us toward high-performance heterojunction crystalline silicon solar cells.

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