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Light-Induced Passivation of Si by Iodine Ethanol Solution

Preprint

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Light-Induced Passivation of Si by Iodine Ethanol Solution

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ABSTRACT

We report on our observations of light-activated passivation (LIP) of Si surfaces by iodine-ethanol (I-E) solution. Based on our experimental results, the mechanism of passivation appears to be related to dissociation of iodine by the photo-carriers injected from the Si wafer into the I-E solution. The ionized iodine (I^-) then participates in the formation of a Si-ethoxylate bond that passivates the Si surface. Experiments with a large number of wafers of different material parameters indicate that under normal laboratory conditions, LIP can be observed only in some samples—samples that have moderate minority-carrier lifetime. We explain this observation and also show that wafer cleaning plays an extremely important role in passivation.

INTRODUCTION

It is well recognized that iodine-ethanol (I-E) or iodine-methanol (I-M) solutions can passivate Si surfaces [1–9]. This method of surface passivation can be very valuable when a temporary and removable passivation of a Si wafer surface(s) is needed. The most common application of a temporary passivation is for making lifetime measurements of Si wafers, where a very high-quality surface passivation is needed to measure the bulk lifetime, τ_b. This is a preferred method of passivation because, unlike other techniques of passivation such as deposition of nitride, oxide, or an n/p junction, I-E passivation is achieved at room temperature without any high-temperature wafer processing. Unfortunately, the mechanism of passivation is not well understood. As a result, it is a common experience that measurements made with I-E (I-M) solution are not reproducible. Earlier studies to investigate sources of these variations have shown that measurement is influenced by wafer cleaning [3,7,10]. Furthermore, Refs. [3,7] have shown that multiple cleaning of wafers leads to an improved passivation. Recently, we developed a procedure for wafer cleaning that yields highly reproducible values of minority-carrier lifetime as measured by photo-conductance decay (PCD) or quasi-steady-state photo-conductance (QSSPC) techniques. This cleaning procedure involves cleaning the wafer in Piranha, followed by a low-temperature oxidation and a hydrofluoric (HF) dip to remove a thin layer from the surface [7].

Because our new procedure enabled reproducible measurement of lifetime, it led to the discovery of another source of variability in lifetime measurement—the influence of light-exposure on the passivation produced by I-E. We observed that surface passivation is greatly hastened if the Si wafer, immersed in I-E solution, is exposed to light [10]. Here, we present a mechanism of passivation by I-E solution, which also explains the results presented in this paper on the dependence of passivation on the light illumination. In particular, we explain a very

intriguing feature as to why only some wafers exhibit light dependence of the measured lifetime on light exposure. We will first briefly describe our experiment approach, including the improved cleaning procedure that has allowed us to achieve repeatable results and concomitantly allowed us to identify the light dependence.

EXPERIMENTAL DETAILS

Surface passivation was determined indirectly through the measurement of the minority-carrier lifetime. It is known that measured lifetime (τ_m) of a Si wafer can be expressed as: $1/\tau_m = 1/\tau_b + SRV/2W$, where τ_b, SRV, and W are the bulk lifetime, surface recombination velocity, and wafer thickness, respectively. Thus, for a given wafer of lifetime τ_b, the measured lifetime depends on the SRV. Because passivation reduces SRV, the passivation effect is manifested as an increase in the measured lifetime. Figure 1 shows effective lifetime, τ_m, for wafers of three different bulk lifetimes (10 µs, 100 µs, and 1 ms) as a function of SRV. It is seen that that the SRV must be reduced to about 1 cm/s to be able to measure the real τ_b of a 1-ms-lifetime wafer. However, for a 10-µs wafer, the SRV on the order of 1000 cm/s is sufficient. Hence, as is generally done, we also used the measurement of τ_m as a parameter to derive the effectiveness of the passivation.

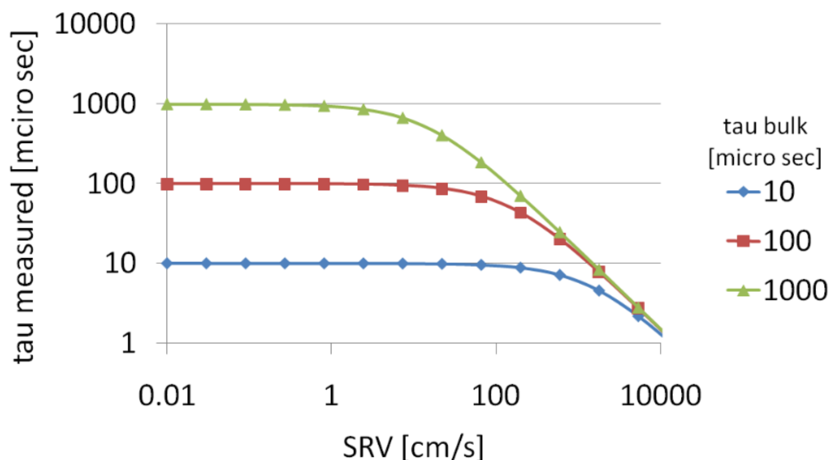

Figure 1. Dependence of measured lifetime, τ_m, on the actual bulk lifetime, τ_b, and surface recombination velocity, SRV.

This work was done primarily using single-side polished, single-crystal wafers within a large resistivity range of 1 Ω-cm to undoped. We used Czochralski (CZ) and float-zone (FZ) grown, both n-type and p-type wafers. The resistivity of each wafer was measured by four-point probe, and wafers were sorted into tight resistivity groups. Samples were cleaned using our recently developed cleaning procedure, placed in a polyethylene bag, and a few drops of I-E solution were placed on each side of the wafer. The bag was then allowed to collapse on the wafer and excess I-E was gently squeezed out. The wafer was then placed in a Sinton apparatus for measurement of τ_m. The Sinton machine allows different modes of measurement, which

include QSSPC, transient PCD, and generalized PC. When calibrated properly, we found that in generalized mode the injection-level dependence of τ_m was the same as measured by other modes. In view of this, we only describe the results measured by generalized PC. Passivation was determined simply on the basis of obtaining the highest lifetime value.

WAFER CLEANING

We (and other researchers) [3,7,10] have shown that wafer cleaning plays a very important role in obtaining good surface passivation. We have determined that even in a very high-quality wafer it is necessary to remove a thin surface layer to get good passivation. We believe that this need arises because some of the impurities diffuse several tens of Å into the surface and that in the presence of impurities it is difficult to get surface passivation that is needed to measure lifetimes > 1 ms. Although one can chemically etch a thin layer from a wafer surface, we found that a low-temperature optical oxidation, followed by an HF dip, can be very useful in removing a controlled layer from the surface. One important question is how deep a surface region must be removed or etched. To answer this question, we performed oxidation in steps to remove only about 75 Å in each step. The sample was cleaned and oxidized before each set of measurements. Figure 2 depicts the time dependence of the lifetime measurements for the first three cleaning steps.

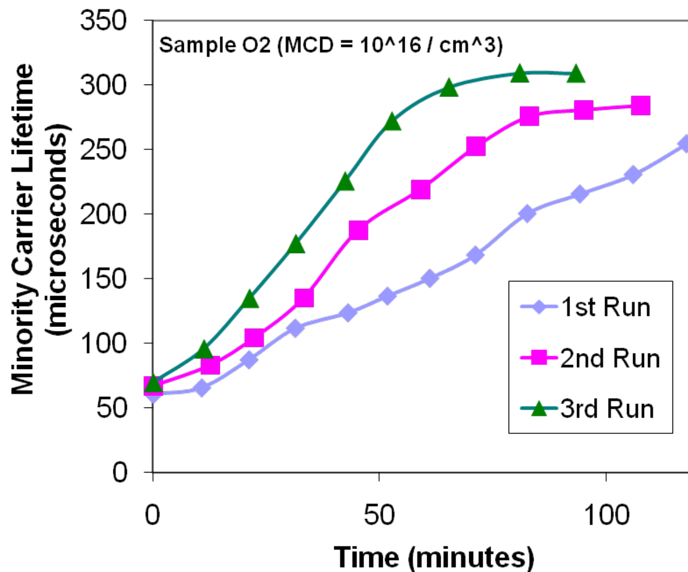

Figure 2. Time-dependence of τ_B after including oxidation in the cleaning procedure, for sequential cleaning steps. Each oxidation run removed a surface layer that was about 75 Å thick.

Figure 2 shows that surface cleanliness and its passivation are a function of total oxidation time. Based on this, we developed our procedure for wafer cleaning that consists of the following: (i) removal of organics by solvent cleaning followed by deionized (DI) water rinse, (ii) piranha (H_2SO_4:H_2O_2 2:1) cleaning at 80°C, (iii) dilute HF rinse, DI water rinse, and nitrogen drying, (iv) oxidation in an optical furnace for 10 min, and (v) dilute HF dip and N_2

drying. Following this cleaning, the samples were placed in a polyethylene bag. We found that zip-lock bags provided an excellent way to passivate the sample. We tried a variety of bags of different qualities and thicknesses, and the most convenient was a 1–2-mil-thick polyethylene bag. A well-cleaned sample was placed in a polyethylene bag and covered on both sides with I-E solution (typically of 0.1 molarity). Excess solution from each surface was squeezed out to leave a thin, uniform layer of the solution on the surface. In our measurements, the change in molarity of the solution between 0.01 and 0.1 did not influence the results. This cleaning-passivating procedure for lifetime measurement works very well and obtains highly reproducible results.

LIGHT-ACTIVATED PASSIVATION

Another feature of Figure 2 is that in each measurement it takes a long time before τ_{max} (maximum value of τ_{m}) is reached. We also observed that if the measurements were done at shorter intervals, the slope of the curves increased. We concluded that the light from the tester itself was influencing the measurement by lowering the surface recombination velocity and concomitantly causing the τ_m to increase. This interesting phenomenon indicates that the I-E surface passivation has a light-activated component. To confirm the light-induced passivation, we cleaned wafers (using our new oxidation procedure), placed them in an I-E bag, and exposed them to about 0.5-sun intensity from a solar simulator for 15 minutes. We found that the lifetime tester yielded τ_{max} immediately after the exposure; furthermore, there was a slow decrease (as shown in Figure 3a). We found that this decrease occurs for all wafers after the measured lifetime reached its maximum (see Figures 3a and 3b).

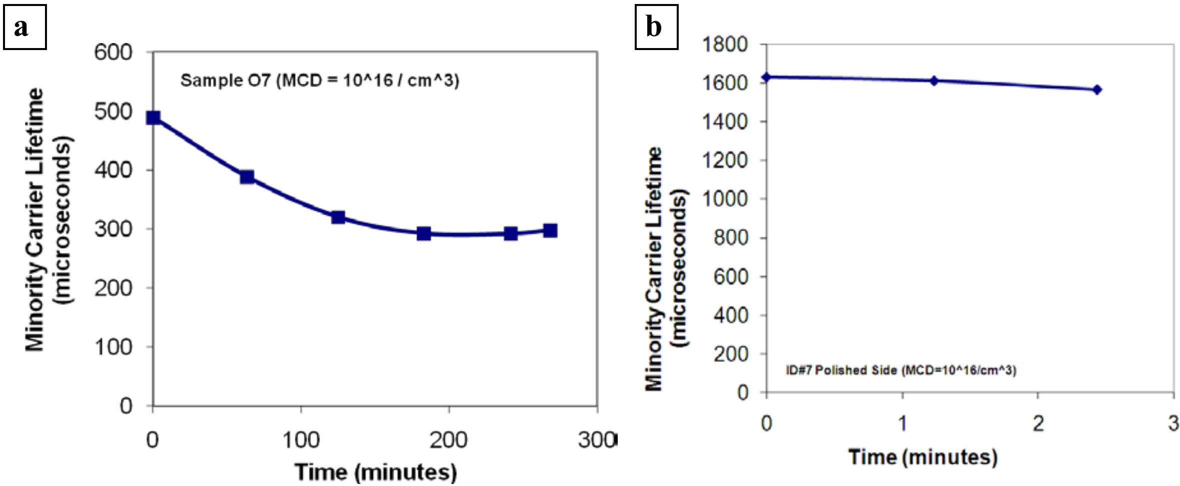

Figure 3. τ_m decay after light exposure in solar simulator (a); the initial increase was not observed. Short-term variation of τ_m for a long-lifetime wafer, (b).

Clearly, the light activation of passivation must be related to the chemistry of I-E. There is some published work [11–13] that proposes that the passivation of the Si surface is caused by tying up of silicon dangling bonds by the ethoxyl group, as illustrated in Figure 4. It has been proposed that this reaction is prompted by the dissociation of iodine.

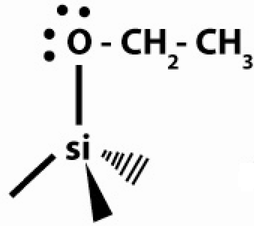

Figure 4. Silicon surface passivated with ethoxylated group.

We first wanted to verify this assumption. To do so, we prepared a set of samples and placed them in a solution containing ethanol only and measured the lifetime. Then these samples were illuminated with light. Next, iodine was introduced, followed by exposure to light from a solar simulator. Figures 5a and 5b show typical results of the two groups. Both samples O3 (which exhibits LIP) and sample X14 (with no LIP effect) show that ethanol alone does not produce any passivation, even with illumination. It is clear that iodine is needed to produce passivation.

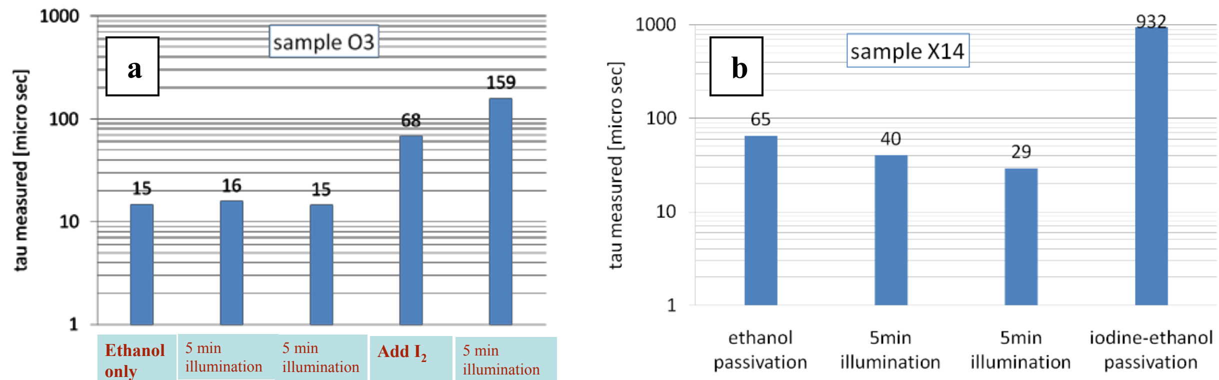

Figure 5. Effect of I_2 and illumination on a medium (a) and high (b) lifetime wafers.

Given that iodine is needed to produce passivation, it is possible that the ultraviolet (UV) component of light can cause dissociation of I_2, and the atomic iodine can further promote formation of Si-ethoxylate bonding. This assumption was tested on several wafers by placing each cleaned wafer in the I-E bag and then exposing it to UV light. However, the lifetime did not reach τ_{max}, as seen in the results of Figure 6. We also tried to determine if the effect was thermally induced because exposure of the wafer in the I-E bag caused it to heat up. Again, heating did not produce any change in the lifetime. Figure 6 elucidates the influence of various treatments on time dependence of the lifetime measured immediately after the treatment.

From the above results it is clear that surface passivation requires the presence of iodine. However, the results of Figure 6 show that iodine in methanol does not appear to dissociate rapidly by UV light, or perhaps there is a need to use higher light intensity. Only some wafers exhibit the effect of light in expediting the passivation process (as described), which suggests that passivation is related to some wafer parameter(s). We have attempted to relate LIP to material properties such as resistivity, oxygen content, carbon concentration, and other impurity levels. In this endeavor, we observed that the LIP effect was displayed by wafers that had τ_b in the range of about 50 to 400 ms (medium-lifetime group). High-lifetime and low-lifetime wafers did not exhibit LIP. This ruled out the association of LIP with Fe.

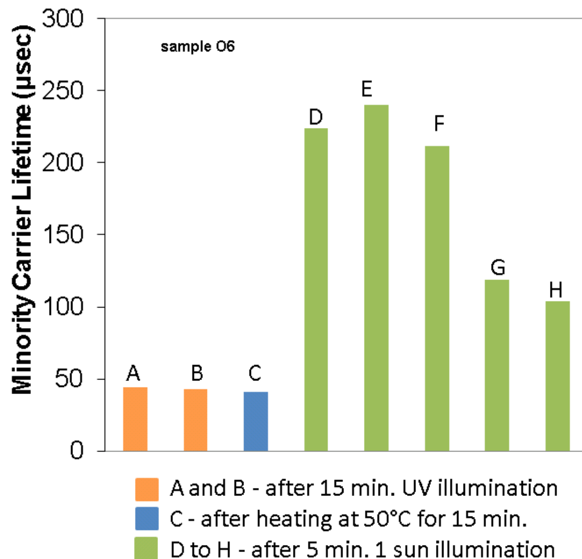

Figure 6. τ_m of a p-type wafer, resistivity 27 Ω-cm measured after several treatments: UV for 15 min and 30 min, heating, exposure to light for different times.

The mechanism of LIP appears to be related to carrier-induced dissociation of I_2. When a wafer in contact with I-E solution is illuminated with light of a broad spectrum, there is a large increase in the minority-carrier concentration at the Si surface. For a p-type wafer, a high concentration of electrons will be available and some of them can be injected into the I-E solution, where they dissociate I_2 producing I^- species. The active I^- can participate in converting a H-terminated surface (produced by HF dip performed just prior to I-E immersion) to an ethoxylate-terminated surface. The kinetics of passivation is illustrated in Figure 7. This reaction occurs in two phases. In phase 1, iodine simply acts as an oxidant. Because iodine is electronegative in nature, it has the ability to take in an extra electron to form ionized atomic iodine, I^-. Thus, when photogenerated electrons are available at the Si-H surface, I_2 can form iodine anions (I^-). The electron flow to iodine leaves Si-H in positively charged $[Si\text{-}H]^+$ ionic form. In this situation, an ethoxyl nucleophile can easily attach itself to Si-H via a coordinate bond, which occurs in the second phase. This occurrence is accompanied by release of hydrogen as a proton from the alcohol, leading to the charge neutrality of the five-coordinate Si species. Formation of five-coordinated Si in aqueous solutions is well known [11–13]. Next, the five-coordinated Si loses an electron, which is captured by iodine, leading to a positively charged five-coordinated Si. In the final step, the loss of another proton results in the formation of the final ethoxylated silicon surface.

The carrier-induced dissociation is likely to depend on the carrier concentration at the surface. The electron density at the surface depends strongly on the bulk lifetime of the wafer and its surface characteristics such as SRV. It is expected that carrier concentration at the surface of a long-lifetime wafer can be orders of magnitude higher than at the surface of a short-lifetime wafer. Hence, a long-lifetime wafer can get passivated even with low-intensity illumination, such as from room light. On the other hand, lower-lifetime material will require longer exposure to light. This explains why in our experiments that long-lifetime wafers, when properly processed, do not need simulator light for passivation. We believe that the same mechanism also applies to short-lifetime wafers.

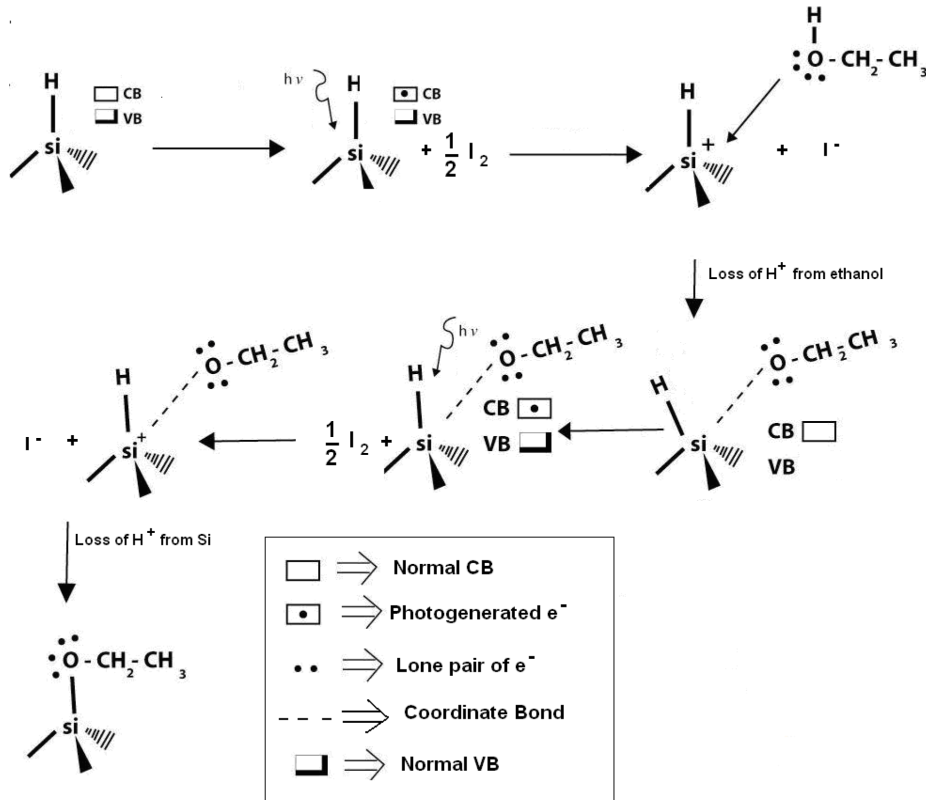

Figure 7. Proposed mechanism for passivation of silicon surface by I-E solution.

CONCLUSIONS

We presented experimental results showing that illumination of a silicon sample embedded in I-E solution causes optically induced enhancement of surface passivation. The mechanism of passivation appears to be related to dissociation of I_2 into I^- ions by the photo-generated carriers. We have proposed a detailed reaction outlining the participation of iodine and photo-generated electrons in producing a passivated Si surface terminated by ethoxylate groups. Our experiments indicate that generally good passivation of silicon wafers requires two essential steps: (i) wafer cleaning, which includes removal of about 200–300 Å of Si from each surface, and (ii) exposure of an I-E-passivated wafer to spectrum-rich light. We outlined a procedure that yields a very clean surface and have found that using fresh chemicals (piranha, HF, and other acids) for each batch of wafers minimizes surface-quality variations. Our experience is that these chemicals have the propensity to acquire impurities from ambient and, in some cases, can leach them from the containers if very high-quality containers are not used. We suggest using optical oxidation after piranha cleaning.

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