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Extremely low surface recombination velocities on crystalline silicon wafers realized by catalytic chemical vapor deposited SiN_x/a-Si stacked passivation layers

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Catalytic chemical vapor deposition (Cat-CVD), also called hot-wire CVD, yields silicon-nitride/amorphous-silicon (SiN_x/a-Si) stacked layers with remarkably low surface recombination velocities (SRVs) of lower than 1.5 cm/s for n-type crystalline Si (c-Si) wafers, and lower than 9.0 cm/s for p-type wafers. The temperature throughout the formation of stacked layers is lower than 250 °C. The usage of a-Si films significantly enhances the effective carrier lifetime of c-Si wafers, and SiN_x films are also essential for reducing SRVs to such low levels. *© 2010 American Institute of Physics*. [doi:10.1063/1.3483853]

Crystalline silicon (c-Si) solar cells require high-quality surface passivation for high conversion efficiency. Sufficient surface passivation is especially necessary for high-efficiency point-contact or back-contact solar cells demanding long-distance diffusion of photogenerated carriers in lateral directions. It is well known that the surface recombination velocity (SRV) of excess carriers can be lowered to the order of cm/s when c-Si surfaces are passivated by thermally-grown silicon-dioxide (SiO_2) films. In particular, a stacked structure consisting of thermally-grown SiO_2 film and plasma-enhanced chemical-vapor-deposited (PECVD) silicon-nitride (SiN_x) film shows excellent passivation ability, with SRVs lower than 2.4 cm/s for a 2.5 Ω cm n-type Czochralski Si wafer.[1] Kerr *et al.* have achieved SRVs of lower than 2.4 and 11.8 cm/s on n- and p-type floating-zone (FZ) c-Si wafers, respectively, by "Alneal," which is annealing at about 400 °C after evaporation of aluminum film on a thermally grown SiO_2 film.[2] However, such remarkable SiO_2 passivation requires processes at temperatures higher than 900 °C. On the other hand, low temperature (<400 °C) passivation techniques are important to prevent the degradation of bulk quality and decrease processing time. Low temperature surface passivation with an SRV of lower than 2 cm/s has been demonstrated by using aluminum-oxide (Al_2O_3) films formed by plasma-assisted atomic layer deposition (ALD) at 200 °C, followed by post-deposition annealing at 425 °C.[3] SiN_x/intrinsic amorphous-silicon (a-Si) stacked layers formed at 50 °C by remote PECVD (RPECVD) yield an SRV of lower than 11 cm/s.[4]

In the present work, we demonstrate improved passivation quality using SiN_x/a-Si stacked layers formed by catalytic chemical vapor deposition (Cat-CVD),[5] often referred to as hot-Wire CVD, which is also a method of forming passivating films at low temperatures. The advantage of Cat-CVD is the absence of damage to Si surfaces from energetic charged species. We particularly investigate the impact of a-Si film thickness and deposition temperatures on passivation. We used 290 μm thick phosphorus-doped n-type (100) FZ-Si wafers with a resistivity of 2.5 Ω cm, and 280 μm thick boron-doped p-type (100) FZ-Si wafers with a resistivity of 2.0 Ω cm. Wafers with mirror-polished surfaces on both sides were used in order to eliminate the effects of surface roughness. All wafers were wet cleaned using 5% diluted hydrofluoric acid to remove native oxide, and then immediately transferred to a load-lock chamber. Two chambers were used for intrinsic a-Si and SiN_x deposition, and wafers were transferred from one chamber to the other via the load-lock chamber. The base pressure in each deposition chamber was below 10^{-5} Pa. a-Si films were deposited on c-Si wafers. The gas pressure during deposition was 0.55 Pa, substrate-catalyzer distance (D_{cs}) 12 cm, silane flow rate 10 SCCM (SCCM denotes cubic centimeter per minute at STP), and the temperature of the tungsten wire used as catalyzer 1800 °C. The thickness of a-Si films (as estimated by an ellipsometer with a helium-neon laser of 632.8 nm wavelength) was controlled in a range up to 50 nm. The deposition rate of a-Si films was around 0.5 nm/s. Substrate temperatures during a-Si deposition were set to either 90 or 150 °C. The thickness of SiN_x was fixed at 100 nm for all experiments presented here. The gas pressure during deposition of SiN_x films was kept at 10 Pa, D_{cs} 8 cm, the substrate temperature at 250 °C, and the catalyzer temperature at 1800 °C. The flow rates of silane and ammonia gases to deposit SiN_x films were 8.5 and 200 sccm, respectively. The refractive index of SiN_x films was 2.00, (measured by spectroscopic ellipsometry). The deposition rate of SiN_x films was 34 nm/min. The effective carrier lifetimes (τ_{effs}) of wafers coated with both SiN_x/a-Si stacked layers and a SiN_x single layer were measured for comparison. The τ_{eff} of passivated Si wafers was characterized at room temperature by a microwave-detection photoconductivity decay (μ-PCD) method, using KOBELCO LTA-1510EP. The excess carriers were generated by a laser pulse whose wavelength was 904 nm and photon density was $5\times10^{13}/cm^2$. The τ_{eff} is determined by the exponential decay of excess carrier concentration.

Figure 1 shows the τ_{eff} of Si substrates passivated by SiN_x/a-Si stacked layers as a function of a-Si film thickness. The τ_{eff} of wafers passivated only by SiN_x films is 210 μs

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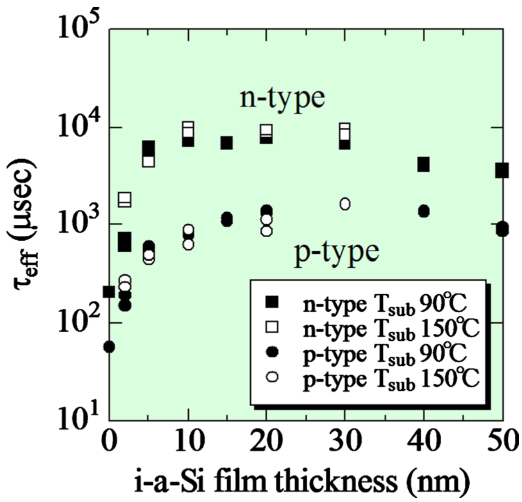

FIG. 1. (Color online) τ_{eff} of Si substrates passivated by a-Si/SiN_x stacked layers as a function of a-Si film thickness.

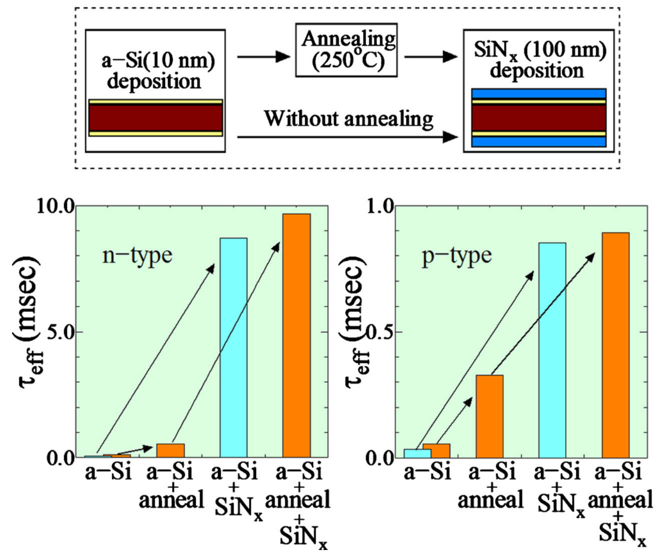

FIG. 2. (Color online) τ_{eff}'s of n- and p-type c-Si wafers passivated by a-Si films with and without annealing at 250 °C, and of a-Si and SiN_x stacked film. The corresponding process flow diagrams are also shown.

for n-type Si and 57 μs for p-type Si. The τ_{eff} tends to increase with the insertion of more a-Si layers. It also increases as the thickness of an a-Si layer increases up to 10 nm, and it reaches maximum values of 9.7 ms for n-type Si and 1.6 ms for p-type Si, suggesting that the inserted Cat-CVD a-Si layers contribute to improved passivating ability. Epitaxial grown c-Si formed during a-Si deposition is known to degrade a-Si/c-Si interface quality.[6] In this study, however, the passivation quality does not appear to change in the range of 90–150 °C. This implies that a-Si layers are not grown epitaxially in this temperature range. Figure 1 clearly shows that τ_{eff} is likely to increase from 210 μs to 9.7 ms as a-Si thickness increases from 0 to 10 nm for n-type wafer. The lower τ_{eff} for a-Si thicknesses less than 10 nm might be due to incomplete a-Si coverage of c-Si surfaces, since some parts of a thin a-Si layer might be etched by hydrogen atoms during successive SiN_x deposition. According to our observations using transmission electron microscope, even c-Si surface is partially etched to a depth of a few nm by initial stage of SiN_x deposition. The surface coverage would be improved by the increase in thickness of the a-Si layer, resulting in the saturation of τ_{eff}. The exact reason for the necessity of a-Si insertion itself is not clear at the moment. However, it is known that direct contact between SiN_x and c-Si makes P-center, which is a defect center caused by nitrogen dangling bonds in Si network.[8] The insertion of a-Si might prevent the generation of such defect centers at the interface.

Figure 2 shows the τ_{eff} of n- and p-type c-Si wafers passivated only by 10-nm-thick a-Si layers and by SiN_x/a-Si stacked layers. We also measured the τ_{eff} of samples in which an annealing process at 250 °C was inserted for 24 min between a-Si and SiN_x deposition. The wafers passivated with a-Si layers without annealing indicate τ_{eff} of below 50 μs, but the τ_{eff} improves up to about 400 μs after annealing at 250 °C. In the case of n-type, further dramatic improvement is realized after the deposition of SiN_x films, resulting in τ_{eff} of as high as 9 ms or more. The same tendency is also confirmed in the case of p-type wafers. These facts indicate that the effect of annealing at 250 °C during SiN_x deposition alone cannot fully explain the realization of such a high τ_{eff}, and the existence of SiN_x films is essential.

The contribution of SiN_x films to improvement in lowering SRVs might be the suppression of recombination on a-Si surfaces. Although small potential barriers for minority carriers exist at a-Si/c-Si interfaces, some minority carriers could reach the a-Si surfaces by tunneling or passing over potential barriers, and recombine at the a-Si surface.[7] SiN_x has high potential barriers, higher than those of a-Si. SiN_x films might significantly passivate the surfaces of a-Si films, resulting in improved τ_{eff}. However, without a-Si, there are many dangling bonds or P-centers at the SiN_x/c-Si interface,[8] as mentioned above. Thus, the insertion of the a-Si layer and successive SiN_x deposition are both very important in reducing dangling bonds and reducing SRVs.

One may think of the effect of the fixed charge in SiN_x as an explanation for the improvement of τ_{eff}.[9] However, as mentioned above, deposition of SiN_x films is effective in improving τ_{eff} for both n- and p-type c-Si wafers. Simple explanation of the phenomena as being due to the fixed charge in SiN_x does not appear acceptable. Passivation effect of SiN_x films on a-Si surfaces still seems to be an attractive explanation in this case.

According to the relation $\tau_{eff}^{-1}=\tau_{bulk}^{-1}+2S/W$, where τ_{bulk}, W, and S represent bulk carrier lifetime, wafer thickness, and SRV respectively, the maximum SRV (S_{max}) can be expressed as $S_{max}=W/2\tau_{eff}$ assuming $\tau_{bulk}=\infty$. The obtained τ_{eff} of 9 ms or more, therefore, corresponds to S_{max} of 1.5 cm/s, which is much lower than the reported SRV of 11 cm/s for c-Si wafers passivated with similar SiN_x/a-Si stacked films deposited by RPECVD.[3] RPECVD (with separation of deposition area from glow-discharge region), can considerably suppress plasma damage on substrates and deposited films, compared with the conventional PECVD. However, the generation of charged species could not be completely suppressed, and the charged species might have negative effects on interface quality. However, in principle, such charged particles are not formed in Cat-CVD, which leads to further improvement in SRVs.

For c-Si wafers suitable for use in solar cells, with resistivity less than 10 Ω cm, passivation using an Al_2O_3 film prepared by plasma-assisted ALD has been the only method to obtain τ_{eff} equivalent to that realized by Cat-CVD

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SiN_x/a-Si stacked passivation.[3] However, according to the report,[3] the ALD requires temperature over 400 °C, and generally, has much lower deposition rate than Cat-CVD. To our knowledge, RPECVD has shown worse passivation results than Cat-CVD. This might be due to the fact that Cat-CVD does not cause plasma damage. Actually, it is known that Cat-CVD a-Si thin-film transistors (TFTs) show better performance than those of PECVD a-Si TFT, and characteristics of Cat-CVD a-Si TFTs are easily degraded by exposure to weak plasma.[10]

In summary, we have demonstrated the superiority of the passivation ability of Cat-CVD SiN_x/a-Si stacked films. An SRV of c-Si wafers of as low as 1.5 cm/s can be realized by using the stacked films formed by Cat-CVD. Such a low SRV appears to be one of the best results ever reported for processing temperatures lower than 250 °C and for c-Si wafers with resistivity less than 10 Ω cm, which are suitable for solar cell fabrication.

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