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Description	

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Drastic reduction in the surface recombination velocity of crystalline silicon passivated with catalytic chemical vapor deposited SiN_x films by introducing phosphorous catalytic-doped layer

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We improve the passivation property of n-type crystalline silicon (c-Si) surface passivated with a catalytic chemical vapor deposited (Cat-CVD) Si nitride (SiN_x) film by inserting a phosphorous (P)-doped layer formed by exposing c-Si surface to P radicals generated by the catalytic cracking of PH_3 molecules (Cat-doping). An extremely low surface recombination velocity (SRV) of 2 cm/s can be achieved for 2.5 Ω cm n-type (100) floating-zone Si wafers passivated with SiN_x/P Cat-doped layers, both prepared in Cat-CVD systems. Compared with the case of only SiN_x passivated layers, SRV decreases from 5 cm/s to 2 cm/s. The decrease in SRV is the result of field effect created by activated P atoms (donors) in a shallow P Cat-doped layer. Annealing process plays an important role in improving the passivation quality of SiN_x films. The outstanding results obtained imply that SiN_x/P Cat-doped layers can be used as promising passivation layers in high-efficiency n-type c-Si solar cells. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4891237]

I. INTRODUCTION

n-type crystalline silicon (c-Si) has recently become more and more attractive to photovoltaic research, raising forecast of switch from p-type to n-type c-Si solar cells on photovoltaic industry.[1,2] Up to date, n-type c-Si solar cells are available, but their market share is at very low level (around 4%).[2] Nevertheless, the highest-efficiency solar cell has been recorded for an a-Si/n-type c-Si heterojunction back-contact solar cell in 2014.[3] n-type c-Si solar cells have many advantages for realizing higher conversion efficiency than p-type wafer cells, such as no light-induced degradation and less effect of metal impurities, and their market share will thus increase in the near future, along with decrease in their process cost.[1,4] Excellent passivation technique is of great importance particularly in improving back-contact c-Si solar cell efficiency. High-efficiency solar cells require surface passivation films not only with high transparency but also with high passivation ability so that photo-generated carriers do not recombine at the c-Si surface.[5] Catalytic chemical vapor deposition (Cat-CVD),[6] also referred to as hot-wire CVD, promises potential applications in passivation technique for c-Si solar cells. The world's best level of an surface recombination velocity (SRV) of 1.5 cm/s has been obtained for n-type c-Si wafers passivated with Cat-CVD SiN_x/amorphous-silicon (a-Si) stacked layers.[7] Cat-CVD can also be used to form a shallow phosphorous (P)-doped layer, called P Cat-doped layer, at a low substrate temperature, such as room temperature.[8,9] The shallow P doped layer can induce field-effect passivation, which can significantly suppress the recombination of minority carriers at c-Si surface. Although the shallow doping can be realized by other techniques, such as plasma doping, atomic layer deposition of dopants, and molecular beam epitaxy,[10–14] Cat-doping can significantly avoid damage onto c-Si surface induced by energetic ions since gas molecules are decomposed on a hot wire by catalytic reaction. The advantage makes Cat-doping become a favorable method for the formation of field-effect passivation layers for c-Si. Regarding the application of P Cat-doped layers to passivation technique, it has been already reported that the addition of P Cat-doped layers can reduce the SRV of n-type c-Si passivated with an a-Si film from 5 cm/s to 3 cm/s.[15] In our previous work, we have optimized SiN_x passivation films with refractive index of ∼2.0 at wavelength of 630 nm prepared by Cat-CVD for n-type c-Si wafers.[16] The highest effective minority carrier lifetime (τ_{eff}) of 3 ms, corresponding to a low SRV of 5 cm/s, can be obtained for n-type c-Si passivated with Cat-CVD SiN_x films deposited at a low substrate temperature (∼100 °C) and post annealing. The use of SiN_x films, whose refractive indexes are adjusted to be 2.0 even after decreasing the substrate temperatures, can avoid optical loss due to parasitic absorption in a-Si for SiN_x/a-Si stacked passivation system. The Cat-CVD SiN_x films with high passivation quality and high transparency are suitable for application to c-Si solar cells. As we mentioned above, a P Cat-doped layer can induce field-effect passivation, which is effective in suppressing surface recombination by sending electrons away from the c-Si surface. In this study, in order to obtain even lower SRV on c-Si surface passivated with a SiN_x film, we attempt to apply P Cat-doping for field-effect passivation. The results obtained show that the passivation quality of the SiN_x/P Cat-doped layer/c-Si structure significantly depends on the amount of activated donors in a P Cat-doped layer. Doped substrate temperature and annealing before depositing SiN_x films are important parameters for

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TABLE I. Sample preparation conditions for P Cat-doping and the deposition of SiN_x and a-Si films.

	Doping	a-Si	SiN_x
Gas sources	PH_3 20 sccm	SiH_4: 10 sccm	SiH_4: 8 sccm NH_3: 150 sccm
Substrate temperature	80–300 °C	90 °C	100 °C
Pressure	1.0 Pa	0.55 Pa	10 Pa
Catalyzer temperature	1300 °C	1800 °C	1800 °C
Time	30–120 s	30 s	184 s

activating P as donors. The deposition of SiN_x films and post annealing at 350 °C for 30 min are necessary to achieve better interface properties and resulting high τ_{eff}.[16] By the field-effect passivation and defect termination by H atoms, τ_{eff} of as high as 7 ms can be obtained, which corresponds to an SRV of ~2 cm/s.

II. EXPERIMENTAL PROCEDURE

Sample preparation conditions are summarized in Table I. All c-Si wafers were first cleaned in diluted (5%) hydro-fluoric acid (HF) solution for 10 s to remove native oxide. P Cat-doped layers, SiN_x films, and a-Si films were prepared in separate Cat-CVD chambers. A 2.25% helium diluted PH_3 was used as gas source for doping process. In this study, we changed the properties of P Cat-doped layers by changing substrate temperature ($T_{s\text{-}dope}$) and doping time (t_{dope}). The deposition condition of SiN_x films and annealing conditions for the samples after depositing the SiN_x films were same as the optimized conditions, under which high τ_{eff} of 3 ms can be obtained for a SiN_x/c-Si structure.[16] 290–μm-thick n-type (100) floating-zone (FZ) Si wafers with a resistivity of 2.5 Ω cm and a bulk minority carrier lifetime of >10 ms were used for the investigation of the passivation quality. The structure for τ_{eff} measurement is shown in Fig. 1. In order to investigate the effect of annealing on passivation quality, the P Cat-doped samples were annealed before and after depositing SiN_x films. In this paper, we refer them to "annealing A" and "annealing B," respectively. Annealing A and annealing B were both conducted in a horizontal tubular furnace in nitrogen atmosphere. We prepared two samples under the same P doping condition at the same batch; one is for a sample with only annealing B, and the other is for a sample with both annealing A and B. The samples without annealing A were passivated with SiN_x films immediately after P Cat-doping without air break, while the samples with annealing A were taken out from the P doping chamber, followed by furnace annealing and then SiN_x deposition without any additional cleaning prior to deposition. All the SiN_x-deposited samples were finally annealed at 350 °C for 30 min (annealing B). The τ_{eff} was measured by microwave photo-conductivity decay (μ-PCD) (KOBELCO LTA-1510EP) using a 904 nm wavelength pulse laser with a photon density of 5×10^{13} cm^{-2}, and then was evaluated from the exponential decay of the microwave reflection intensity. The τ_{eff} was measured in position-dependent mapping mode, and τ_{eff} shown below is the maximum value in the 20×20 mm^2 area mapping. The relationship between τ_{eff} and SRV is described as

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2SRV}{W}, \quad (1)$$

where τ_{bulk} and W represent minority carrier lifetime in bulk c-Si and wafer thickness, respectively. In this study, we calculated SRV by assuming $\tau_{bulk} = \infty$. We also measured excess-carrier-density-(Δn-) dependent τ_{eff} by quasi-steady-state photoconductance (QSSPC) (WCT-120, Sinton Instruments).

We employed the Hall effect measurement to evaluate the sheet carrier density (N_D) of doped samples and secondary ion mass spectrometry (SIMS) for P concentration. The properties of c-Si wafers used for SIMS measurement are same as those used for τ_{eff} measurement. The SIMS measurement was performed from the back side of the samples after removing most of Si wafers in order to avoid the effect of knock-on and resulting unintentional broadening of P profiles. We used 2900 Ω cm p-type FZ c-Si wafers for the Hall effect measurement. The capture of carriers at defects on c-Si surface and oxidization may affect significantly the results of the Hall effect measurement.[8,17,18] In order to prevent these effects, a 10-nm-thick a-Si film was deposited on c-Si immediately after P doping without air exposure. In order to know the effect of annealing on N_D, samples were annealed at 350 °C before and after depositing a-Si films. Four Al electrodes were formed by evaporation through a metal hard mask to form the van der Pauw configuration. The samples were annealed at 350 °C for 1 min to make Ohmic contact between Al electrodes and a P Cat-doped layer. Figure 2 shows the cross-sectional schematic of a sample for the Hall effect measurement. The details of the measurement have been described in Ref. 8. The effect of H etching on the

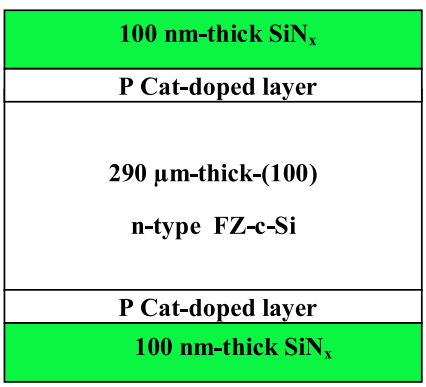

FIG. 1. The cross-sectional schematic of a sample for τ_{eff} measurement.

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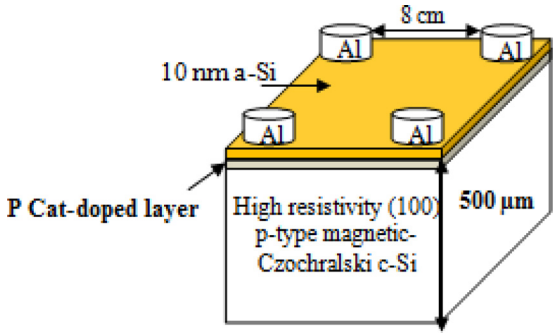

FIG. 2. The cross-sectional schematic of a sample for Hall measurement.

morphology of c-Si surface after P Cat-doping was evaluated by atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

A. The effect of annealing on P activation as donors and the passivation characteristic of SiN_x/P Cat-doped layer/c-Si structures

Annealing plays an important role in improving the passivation quality of SiN_x/c-Si structures.[16,19,20] In this study, we first investigate the effect of annealing. c-Si wafers received P Cat-doping at a $T_{s\text{-}dope}$ of 80 °C for 1 min, followed by SiN_x film deposition. The samples were then annealed (annealing B) at various annealing temperatures (T_{aB}) for 30 min. Figure 3 shows the dependence of τ_{eff} of a SiN_x/P Cat-doped layer/c-Si structure on T_{aB}. The τ_{eff} of SiN_x/c-Si structures as a function of T_{aB} is also shown for comparison. τ_{eff} starts to increase when T_{aB} exceeds 200 °C for both structures. τ_{eff} reaches the highest value at a T_{aB} of 350 °C, and then decreases with further increase in T_{aB}. The improvement in the τ_{eff} of the SiN_x/c-Si structure is supposed to be due to the effect of defect termination by H atoms during annealing.[16,19–21] For a SiN_x/P Cat-doped layer/c-Si structure, passivation quality relies not only on H defect termination but also on field-effect passivation, and increase in T_{aB} might lead to increase in donor (activated P) concentration and resulting enhancement in field-effect passivation. Hayakawa *et al.* have reported that the most inactivated P atoms in a P Cat-doped layer exist in the forms of chemisorbed PH-, PH_2-, and PH_3 (coordinate bond)-type bonds with Si atoms, denoted as PH_x (x = 1–3).[8] It has been reported that P and H atoms are major products, while PH- and PH_2- are minor products in the catalytic decomposition of PH_3.[22] We thus guess that the extraction of H atoms from PH_3 molecules by formation of H_2 molecules or the addition of H atoms to P atoms on a c-Si surface is possible mechanisms of PH_x production.

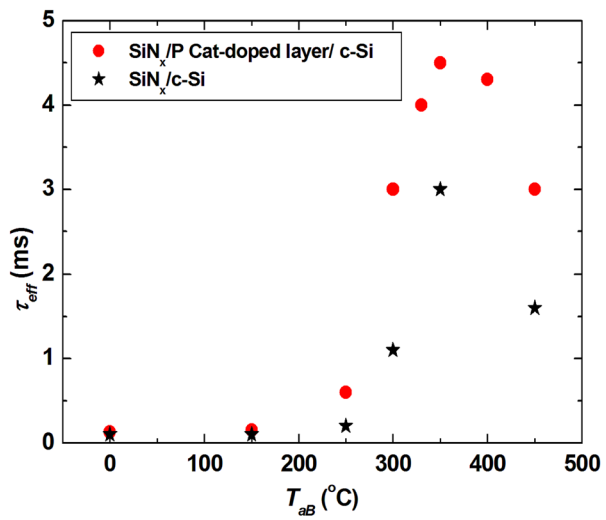

FIG. 3. The dependence of SiN_x/P Cat-doped layer/c-Si structures on T_{aB} at an annealing time of 30 min. τ_{eff} of SiN_x/c-Si structures as a function of T_{aB} is also shown for comparison.

PH_x may decompose at high temperature, resulting in the release of P and H atoms. The released H atoms can diffuse to c-Si surface and terminate defects there, and the released P atoms act as donors and contribute to reinforcing field-effect passivation. There have been a number of literatures about the decomposition of P-H bonds using samples with PH_3 adsorbed on c-Si (100).[23–26] Yu *et al.* have reported that PH_3 molecules are partially dissociated at an annealing temperature of 275 °C for PH_3 adsorbed samples.[23] Tsai *et al.* have reported that PH_3 species are converted to PH_2 species in an adsorbed layer at annealing temperature >317 °C, and a P-H peak disappears when an annealing temperature exceeds 377 °C.[25] These facts indicate that PH_2 species are decomposed to P and H atoms at around 300 °C. We can guess that the released H atoms can make bonding with Si atoms and P atoms start to act as donors. In this study, as has been shown in Fig. 3, the τ_{eff} of a SiN_x/P Cat-doped layer/c-Si structure is much higher than that of SiN_x c-Si structure when $T_{aB} \geq 250$ °C. This fact suggests that PH_x starts to decompose efficiently at a T_{aB} of 250 °C. This temperature is quantitatively consistent with the values of the literatures shown above. A T_{aB} of 350 °C is sufficiently high for both PH_x bond breaking in a P Cat-doped layer and defect termination by H in SiN_x films, and higher T_{aB} leads to the desorption of H atoms to atmosphere and resulting in the decrease of τ_{eff}. The highest τ_{eff} can thus be obtained at a T_{aB} of 350 °C for both structures.

On the other hand, contrary to our expectations, the results of the Hall effect measurement show that N_D decreases by annealing. N_D is $1.2 \times 10^{12}\,cm^{-2}$ before annealing, while it reduces to $0.9 \times 10^{12}\,cm^{-2}$ for samples with annealing at 350 °C for 30 min after depositing a-Si films, and to $0.7 \times 10^{12}\,cm^{-2}$ for samples with annealing at the same condition before depositing a-Si films. For the sample annealed after depositing an a-Si film, a possible reason for reduction in N_D is the diffusion of H atoms from the a-Si film to the P Cat-doped layer, which can cause the formation of more PH_x than PH_x decomposition in a P Cat-doped layer and resulting reduction in N_D. Lower N_D obtained in the sample annealed before depositing an a-Si film may be due to the oxidization of c-Si surface. In order to conduct annealing process, we have to take out the samples to atmosphere. Oxidation can inactivate P at surface c-Si and/or induce the formation of a thin Si oxide film containing P atoms on c-Si surface, which affect the results of the Hall effect measurement. In order to clarify this effect, the samples for the Hall effect measurement

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after P Cat-doping at 350 °C were put in air for 15 min before depositing a-Si films. By the additional air exposure, N_D drops from 3×10^{12} to $0.5 \times 10^{12}\,cm^{-2}$, which is a clear evidence of oxidation-induced reduction in N_D. We actually confirmed the formation of a SiO_x film with a thickness of 1.1 nm and a refractive index of 1.5 at a wavelength of 630 nm on c-Si surface by using spectroscopic ellipsometry.

However, the oxidation of c-Si surface does not deteriorate the passivation quality of SiN_x/P Cat-doped layers on c-Si structure. The P Cat-doped layer/c-Si structures with or without annealing A (at 350 °C for 30 min) were put in air for one week. The sample was then passivated with a SiN_x film, and annealed at 350 °C for 30 min (annealing B). For the sample without annealing A, τ_{eff} obtained of 4.4 ms does not differ from τ_{eff} of sample without air exposure. For the sample annealed with annealing B, τ_{eff} obtained is 6.4 ms. The addition of annealing A rather improves the passivation quality of a SiN_x/P Cat-doped layer structure by oxidation. We also investigated the effect of oxidation on τ_{eff} of SiN_x-passivated c-Si samples. Some c-Si wafers received annealing A at 350 °C for 30 min in N_2 atmosphere. The τ_{eff} of SiN_x/c-Si structures increases from 50 to 100 μs for samples without annealing B and from 3 to 3.5 ms for samples with annealing B. This indicates that the thermal oxidation of c-Si surface slightly improves the passivation quality of SiN_x films on c-Si wafers. This improvement may be due to reduction in interface state by the formation of a SiO_x film.[27–29] Furthermore, τ_{eff} of 250 μs is obtained for SiN_x/P Cat-doped layer/c-Si structure with only annealing A. This value is higher than that of a SiN_x/c-Si structure annealed with only annealing A. This result indicates that despite reduction in N_D by oxidation, improvement in interface quality by oxidation and defect termination by H atoms released from PH_x can contribute to increase in τ_{eff}. After annealing B, besides the effect of defect termination by H atoms diffused from a SiN_x layer, more PH_x in a P Cat-doped layer can be decomposed, leading to higher donor concentration and more effective defect termination by H atoms, which results in higher τ_{eff}.

On the other hand, as mentioned previously, N_D obtained for an a-Si/P Cat-doped layer/c-Si structure is reduced by annealing at 350 °C for 30 min. Cat-CVD SiN_x films also contain high amount of H atoms, which can diffuse from SiN_x films to c-Si surface and terminate defects or recombine with P atoms to form more PH_x during annealing B. Assuming that reduction in N_D for the SiN_x/P Cat-doped layer/c-Si structures is the same as the case of a-Si/P Cat-doped layer/c-Si after annealing B, N_D of a SiN_x/P Cat-doped layer/c-Si structure decreases by 25%. The sample undergoing both annealing A and B has N_D of $\sim 5 \times 10^{11}\,cm^{-2}$, which is due to the effect of oxidation by annealing A and H diffusion during annealing B. This value of N_D might be high enough for field-effect passivation. The fact that the N_D of the sample receiving both annealing A and B is less than that with only annealing B indicates less effective field-effect passivation. However, the benefit of defect termination by H atoms might overcome the deterioration of field effect and lead to better τ_{eff} for the sample with both annealing A and B.

To understand the effect of annealing A on the passivation quality of SiN_x/P Cat-doped layers, c-Si samples Cat-doped at 80 °C for 1 min were annealed (annealing A) at various annealing temperatures (T_{aA}) for 30 min in the tubular furnace. Samples were then moved to the Cat-CVD system to deposit SiN_x films. Finally, samples were annealed at 350 °C for 30 min (annealing B). Figure 4 shows the τ_{eff} of SiN_x/P Cat-doped layer/c-Si structures after annealing A and B as functions of T_{aA} and annealing time (t_{aA}) for annealing A. N_D as a function of T_{aA} is also shown. One can clearly see that τ_{eff} increases with T_{aA} for samples both with and without process B. τ_{eff} increases when T_{aA} increases and decreases for $T_{aA} \geq 400$ °C. This is probably due to increase in N_D at higher T_{aA}. The increase in N_D is probably due to the decomposition of PH_x at higher T_{aA} and resulting activation of higher amount of P atoms. Additionally, the thermal oxidation of c-Si surface for the samples annealed at high temperature and defect termination by H atoms by annealing might contribute to the formation of a high-quality SiN_x/SiO_x/P Cat-layer and c-Si interface, resulting improvement in τ_{eff}. Because the P Cat-doped layer is very shallow, too high T_{aA} might lead to the desorption of H and P atoms to environment, which can result in decrease in τ_{eff} due to less effective defect termination and field-effect passivation. The complete

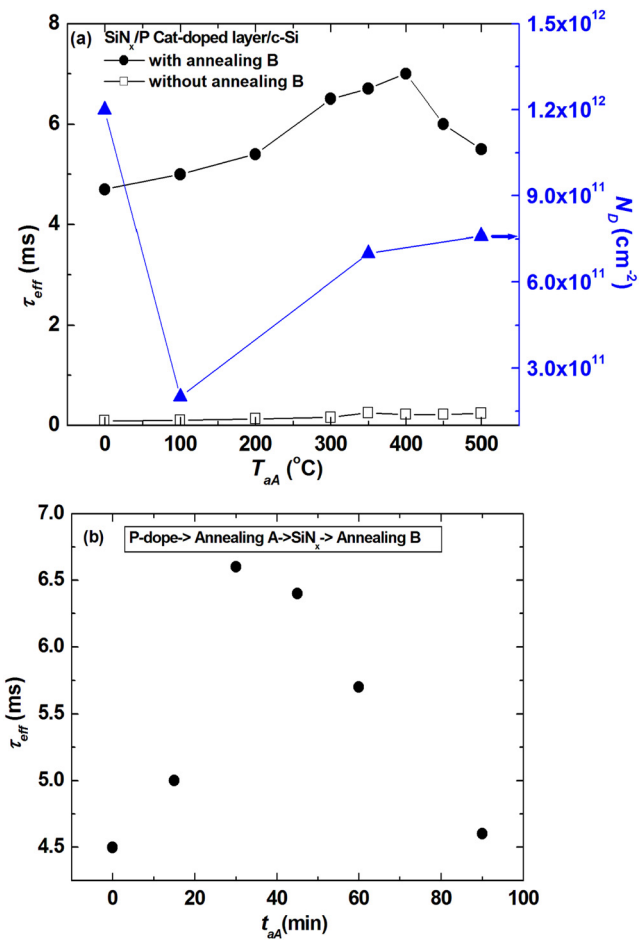

FIG. 4. τ_{eff} of SiN_x/P Cat-doped layer/c-Si structures after annealing A at various T_{aA} for 30 min and t_{aA} at a T_{aA} of 350 °C. Annealing B was conducted at 350 °C for 30 min.

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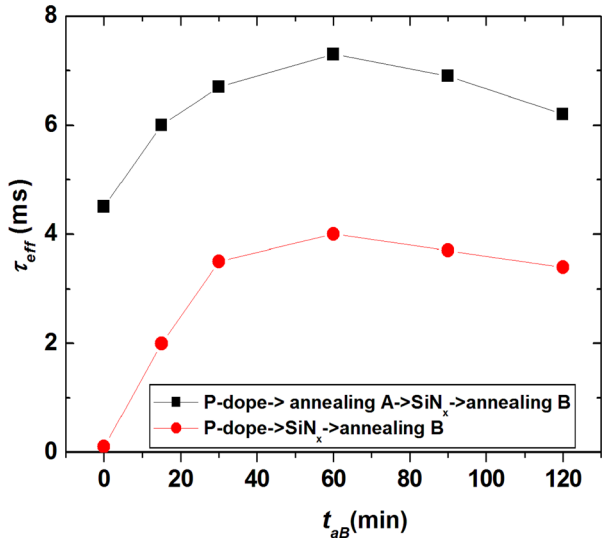

FIG. 5. τ_{eff} of SiN_x/P Cat-doped layer/c-Si structures with and without annealing A as a functions of t_{aB} at a T_{aB} of 350 °C. Annealing A was conducted at 400 °C for 30 min.

thermal desorption of P atoms from PH_3 adsorbed c-Si surface at high temperature above 550 °C was also reported in Ref. 24, in which the desorption of H atoms at 400 °C has also been observed. The same tendency is seen in the annealing time dependence for annealing A, as shown in Fig. 4(b). T_{aA} of 400 °C and t_{aA} of 30 min are thus optimum conditions for annealing A needed to activate P in P Cat-doped layer without H and P desorption, and the highest τ_{eff} obtained for SiN_x/P Cat-doped layer/c-Si structures under the conditions. Figure 5 shows τ_{eff} as a function of the duration of annealing B (t_{aB}). We can see that τ_{eff} is still high for long t_{aB}. The tendencies of the variation of τ_{eff} for both samples are the same. Annealing for 30 min is enough to obtain high passivation quality for the samples. Further increase in t_{aB} does not enhance more the activation of P atoms as well as defect termination. The instability of τ_{eff} due to increase in T_{aB} and t_{aB} may raise a doubt of reduction in τ_{eff} after long time exposure to air even at room temperature. We have confirmed that τ_{eff} of both SiN_x/c-Si and SiN_x/P Cat-doped layer/c-Si structures remain original values even after putting in air at room temperature for about 10 months.

In summary, a remarkably high τ_{eff} of ~7 ms, which corresponds to an SRV of ~2 cm/s, can be achieved for SiN_x/P Cat-doped layer/c-Si samples after annealing A and B. Compared with a SiN_x/c-Si structure, the insertion of P Cat-doped layer can reduce an SRV from 5 cm/s to 2 cm/s. The SRV of 4 cm/s has also been achieved when nearly stoichiometric SiN_x films were deposited by plasma-enhanced CVD (PECVD) on 150–μm-thick 3–5 Ω cm n-type Czochralski (Cz) Si wafers after annealed in an industrial firing process.[30] An SRV of lower than 10 cm/s has been reported for 1.5 Ω cm p-type Si wafers passivated with stoichiometric SiN_x films.[31] In these reports, they calculate SRV through τ_{eff} obtained by a contactless photoconductance tester allowing both transient PCD and QSSPC measurements at an Δn of 1×10^{15} cm^{-3}. Figure 6 shows τ_{eff} of a SiN_x/P Cat-doped layer/c-Si structure and a SiN_x/c-Si structure measured by QSSPC in transient mode. We observed τ_{eff} of ~7 ms for SiN_x/P Cat-doped layer/c-Si structure and ~3 ms for SiN_x/c-Si structure at a Δn of 2.4×10^{14} cm^{-3}. At a Δn of 1×10^{15} cm^{-3}, τ_{eff} is ~4 and 1.8 ms for SiN_x/P Cat-doped layer/c-Si and SiN_x/c-Si structures, corresponding to SRVs of 3.6 and 8 cm/s, respectively. Our SRV obtained in this study is the lowest level for n-type c-Si passivated with SiN_x films without firing process or with only low temperature process, which is acceptable for fabrication of a-Si/c-Si hetero-junction solar cells. The remarkable value of our SRV obtained for SiN_x/P Cat-doped layer/c-Si structure highlights the promising application of Cat-CVD technique in high-efficiency n-type c-Si based solar cell fabrication.

B. Effect of $T_{s\text{-}dope}$ and doping duration on the passivation characteristic of SiN_x/P Cat-doped layer/c-Si structure

High $T_{s\text{-}dope}$ can activate P atoms as donors in a P Cat-doped layer.[8,9] This can contribute to improvement in field-

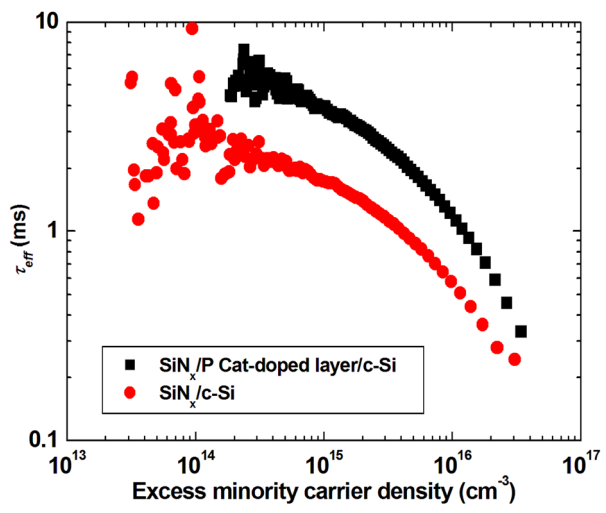

FIG. 6. τ_{eff} as a function of excess carrier density in a SiN_x/P Cat-doped layer/c-Si structure and a SiN_x/c-Si structure.

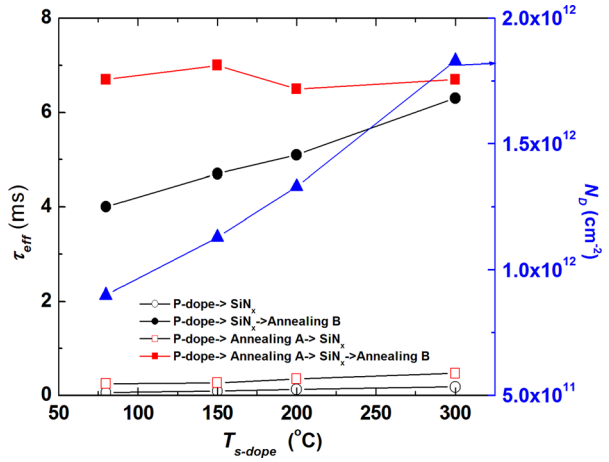

FIG. 7. τ_{eff} of SiN_x/P Cat-doped layer/c-Si samples as a function of $T_{s\text{-}dope}$. N_D as a function of $T_{s\text{-}dope}$ before annealing A is also shown. Annealing A was conducted at 400 °C for 30 min and annealing B was conducted at 400 °C for 30 min.

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effect passivation. In this investigation, we prepared P Cat-doped samples at various $T_{s\text{-}dope}$ for 1 min. Figure 7 shows τ_{eff} of SiN_x/P Cat-doped layer/c-Si samples as a function of $T_{s\text{-}dope}$ with and without annealing A. N_D as a function of $T_{s\text{-}dope}$ before annealing is also shown. N_D increases with increase in $T_{s\text{-}dope}$. This may suggest that H atoms desorb from c-Si surface during P Cat-doping at high $T_{s\text{-}dope}$ due to the extraction of adsorbed H atoms on c-Si surface by atomic H and/or PH_3.[8,32,33] As we mentioned above, Umemoto *et al.* have reported that major products in the catalytic decomposition of PH_3 molecules on a heated tungsten catalyzer are P and H atoms.[22] Here, we suppose that the reaction of atomic H with adsorbed H and/or PH_x on a c-Si surface and/or PH_x bond breaking are possible mechanisms for H release at high $T_{s\text{-}dope}$. This process might assist P activation. We can see lower H concentration in a sample doped at a $T_{s\text{-}dope}$ of 300 °C in a SIMS profile, as shown in Fig. 8 later. The increase in N_D makes small increase in τ_{eff} before annealing. It contributes significantly to improvement in τ_{eff} for the sample doped at high $T_{s\text{-}dope}$ when the samples were annealed with annealing B. The samples doped at a $T_{s\text{-}dope}$ of 300 °C, which shows N_D of $\sim 2\times10^{12}\,cm^{-2}$, can reach the highest τ_{eff} of ~6 ms.

Figure 7 also shows τ_{eff} of SiN_x/P Cat-doped layer/c-Si samples with annealing A and B as a function of $T_{s\text{-}dope}$. One can see that τ_{eff} does not depend on $T_{s\text{-}dope}$, and all the

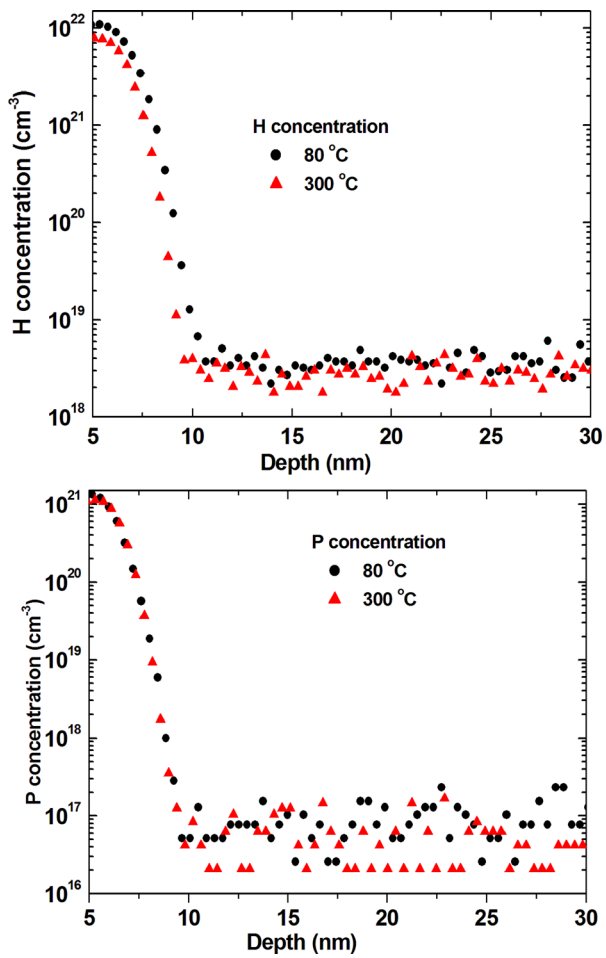

FIG. 8. SIMS profiles of P and H atoms in the samples doped at 80 °C and 300 °C without annealing.

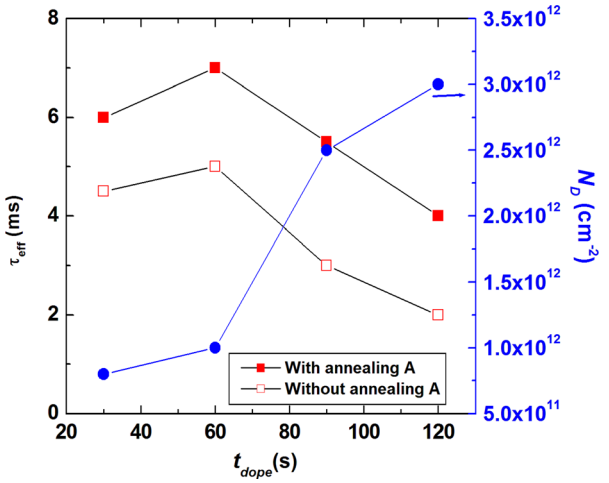

FIG. 9. τ_{eff} of SiN_x/P Cat-doped layer/c-Si samples as a function of t_{dope} with and without annealing A. N_D before annealing is also shown. Annealing A was conducted at 400 °C for 30 min and annealing B was conducted at 400 °C for 30 min.

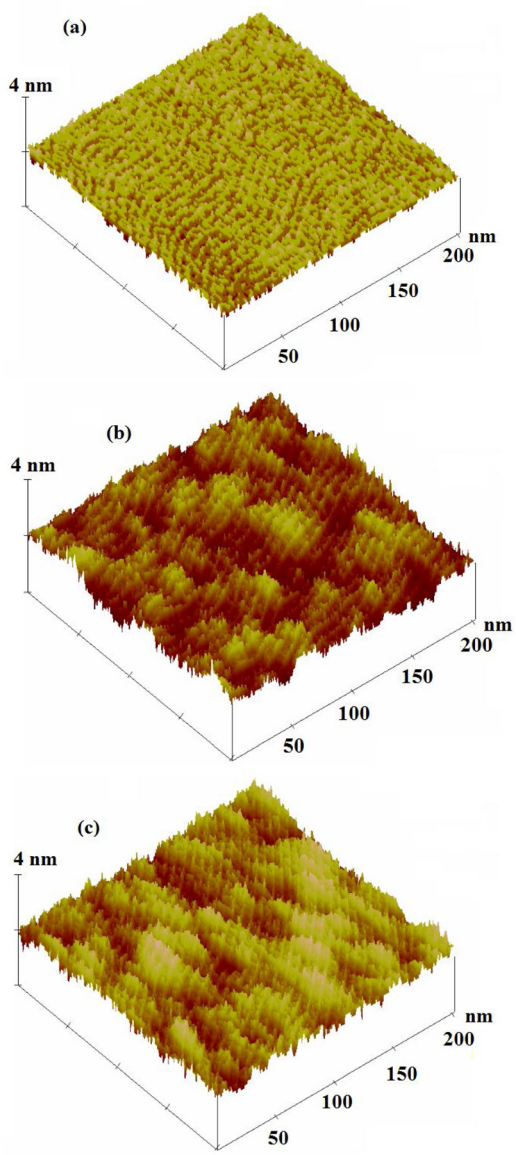

FIG. 10. Surface AFM images of (a) bare c-Si and c-Si Cat-doped for (b) 60 s and (c) 90 s.

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samples have constant and high τ_{eff} of 7 ms. This result suggests that P donor concentration is constant in all the samples with annealing before and after SiN_x deposition. Figure 8 shows the SIMS profiles of samples with P Cat-doping at $T_{s\text{-}dope}$ of 80 and 300 °C before annealing. We can see no significant difference in the two profiles, suggesting that the activation ratio of P atoms in the two samples is similar.

N_D of a P Cat-doped layer also increases with t_{dope}.[9] We should therefore concern the effect of doping time on τ_{eff} of SiN_x/P Cat-doped layer/c-Si samples. The samples were doped at 80 °C for 30, 60, 90, and 120 s. The effect of annealing before depositing SiN_x films was also investigated for these samples. Figure 9 shows the τ_{eff} of SiN_x/P Cat-doped layer/c-Si samples as a function of t_{dope} with and without annealing A. N_D without annealing is also shown. Although N_D increases with increase in t_{dope}, τ_{eff} decreases when $t_{dope} \geq 60$ s. For the sample doped for 30 s, τ_{eff} is low due to low N_D. A possible reason for the low τ_{eff} observed in the samples with $t_{dope} \geq 60$ s is the effect of surface etching by radical species during Cat-doping process. Figure 10 shows the surface AFM images of bare c-Si and c-Si doped for 60 s and 90 s. The surface of bare c-Si has a root-mean-square roughness (R_{rms}) of ~0.09 nm with the average height of 0.3 nm. As shown in Figs. 10(b) and 10(c), the two P Cat-doped samples have more roughened surfaces, and the surface receiving longer Cat-doping is more seriously etched. The sample with a t_{dope} of 90 s has a R_{rms} of 0.24 nm and average height is 0.9 nm, while they are 0.21 nm and 0.7 nm, respectively, for the sample doped at 60 s. Excess t_{dope} thus rather deteriorates the interface quality, and an optimum t_{dope} exists to obtain high τ_{eff} for SiN_x/P Cat-doped layer/c-Si structure.

IV. CONCLUSION

In conclusion, an extremely low SRV of 2 cm/s can be obtained for the SiN_x/P Cat-doped layer/n-c-Si structure. Annealing plays important roles for improving the passivation quality of SiN_x films and enhancing field-effect passivation. Additional annealing, before depositing SiN_x films (annealing A), enhances the activation of P dopants in a P Cat-doped layer and improves τ_{eff}. Increase in $T_{s\text{-}dope}$ increases sheet carrier density, resulting in the improvement of τ_{eff}. τ_{eff} of SiN_x/P Cat-doped/c-Si sample decreases with excessive t_{dope} due to etching effect by radical species during P Cat-doping. An SRV of 2 cm/s is obtained under optimum Cat-doping and annealing conditions for SiN_x films on n-type c-Si wafers, indicating the potential application of Cat-CVD in producing high-efficiency c-Si solar cells. We emphasize that the use of a high transparent SiN_x passivation layer with a P Cat-doped layer can enhance the performance of n-type c-Si solar cells, particularly of back-contact solar cells.

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