

## Metastable effects in hydrogenated amorphous silicon–silicon nitride multilayers

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The metastable effects arising from bias voltage, light illumination, and thermal quenching in hydrogenated amorphous silicon–silicon nitride ( $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$ ) multilayers have been studied. The coplanar conductance increases with bias voltage at moderately high voltages and decreases after bias stressing even at room temperature. After a brief light illumination, upon which the Staebler-Wronski defect is hardly created, we observed persistent photoconductivity (PPC) and an increase of sub-band-gap absorption in the multilayers. Annealing above the film deposition temperature decreases the PPC effect, but the increase of the sub-band-gap absorption for the PPC state is observed, indicating that the PPC effect is correlated with an increase of the gap state near the interfaces. We also observed an excess conductivity in the intentionally nitrogen-contaminated  $a\text{-Si:H}$  film by light illumination at an elevated temperature. Contrary to an unlayered intrinsic  $a\text{-Si:H}$ , the conductivity of a multilayered film increases upon thermal quenching. A possible model is proposed to explain the metastable effects in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers.

### I. INTRODUCTION

It has been discovered that amorphous semiconductors can be prepared in multilayered structures or superlattices with uniform layers and relatively abrupt interfaces.<sup>1</sup> The stringent requirement for lattice matching in crystalline superlattices is relaxed in the amorphous case because of the nonperiodic structure and the ability of hydrogen to passivate defects. The lack of this requirement for lattice matching allows us to fabricate various multilayers, including hydrogenated amorphous silicon–silicon nitride ( $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$ ),<sup>1–4</sup> ( $a\text{-Si:H}/a\text{-SiO}_x\text{:H}$ ),<sup>5</sup> ( $a\text{-Si:H}/a\text{-SiC}_x\text{:H}$ ),<sup>4,6</sup> and ( $a\text{-Ge:H}/a\text{-Si:H}$ ).<sup>1,7</sup>

These amorphous superlattices exhibit many interesting properties similar to crystalline ones, for example, the quantum-size effect<sup>1–3</sup> and space-charge doping.<sup>3,4</sup> The presence of two-dimensional minibands has been directly identified in the resonance tunneling characteristics of  $a\text{-SiN}_x\text{:H}/a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  double-barrier diodes<sup>8</sup> and in the differential optical absorption spectra of  $a\text{-Si:H}/a\text{-SiC}_x\text{:H}$  multilayers.<sup>9</sup> Interfaces between amorphous semiconductor materials are present in a wide variety of electronic devices. The multilayers provide an opportunity to study the interface between two amorphous semiconductors because of the large number of interfaces. Roxlo and Abeles<sup>10</sup> observed the built-in electric fields of up to  $4 \times 10^5$  V/cm, corresponding to an interface charge density of at least  $3 \times 10^{12}$  cm<sup>-2</sup>, in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers. Infrared spectroscopy shows  $10^{15}$  cm<sup>-2</sup> extra hydrogen atoms at the interface.<sup>11</sup> This hydrogen relieves the large lattice mismatch between the two layers and pacifies the defects.

On the other hand, the anomalous metastable effects, such as persistent photoconductivity<sup>12–14</sup> (PPC) having a

lifetime of the order of days and bias-induced enhancement<sup>15</sup> in the coplanar conductance, were reported in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayer films. The PPC effect has also been observed in doping-modulated  $n\text{-p-n-p}$   $a\text{-Si:H}$  multilayers<sup>16</sup> and unlayered compensated  $a\text{-Si:H}$ .<sup>17,18</sup> The generation process of the PPC in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers is thermally activated and the effect anneals away above 130°C. The PPC in this multilayered film has not been understood yet, although a few models<sup>12,19</sup> were proposed.

In this work, we present the metastable effects arising from bias voltage, light illumination, and thermal quenching in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers. The sub-band-gap optical absorption coefficients increase after a brief white-light illumination which gives rise to the large PPC and to the negligible light-induced defect creation. Annealing above the deposition temperature significantly reduces the PPC effect, and we found that the coplanar conductivity increases after rapid cooling from above 180°C, as in doped  $a\text{-Si:H}$ . Based on our experimental results, we propose a model to explain the metastable effects in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers.

### II. EXPERIMENTAL DETAILS

The amorphous films were deposited on Corning 7059 glass substrates heated to 250°C by rf glow discharge decomposition of silane ( $\text{SiH}_4$ ) mixtures. For preparing the  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayered samples, the composition of the reactive gases was altered periodically between  $[\text{SiH}_4] + 8[\text{H}_2]$  and  $[\text{SiH}_4] + 7[\text{NH}_3] + 8[\text{H}_2]$ , while the plasma was maintained continuously. The deposition rate was chosen to be small enough ( $\sim 0.3$  Å/sec) by  $\text{H}_2$  dilution. This deposition technique gives the remnant ni-

trogen in the  $a$ -Si:H layer, but the N incorporation can be minimized by decreasing the deposition rate.

The electrical measurements were made along the film plane (coplanar) using evaporated Al contacts. Before evaporating electrodes, the rectangular multilayered films of  $0.6 \times 0.12 \text{ cm}^2$  in the top area were formed by dry etching in order to assure that electrical contact could be made to all individual layers.

Before measurements, the samples were annealed at  $180^\circ\text{C}$  in a vacuum for 1 h in order to remove the surface adsorbates and the residual light-induced effect. The temperature dependence of conductivity was measured while increasing the temperature ( $\sim 4^\circ\text{C}/\text{min}$ ) after cooling the sample to room temperature. Optical illumination was performed using a tungsten-halogen lamp with an intensity of  $50 \text{ mW}/\text{cm}^2$ . And the sub-band-gap absorption was measured by a constant photocurrent method (CPM). For measurements of thermally induced changes, rapid cooling was performed by flowing water into the substrate holder. The cooling rate was approximately  $5\text{--}10^\circ\text{C}/\text{sec}$  for rapid cooling and  $\sim 2^\circ\text{C}/\text{min}$  for slow cooling.

### III. EXPERIMENTAL RESULTS

We have prepared many  $a$ -Si:H/ $a$ -SiN<sub>x</sub>:H multilayered films with various sublayer thicknesses. All multilayers exhibit a metastable effect, but we report only on the sample consisting of  $a$ -Si:H and  $a$ -SiN<sub>x</sub>:H of 25 and 40 Å each in thickness, with periods of 100. As the number of interfaces is decreased, the metastable effects in the multilayers with a fixed total thickness might be decreased. The optical gap of  $a$ -Si:H(25 Å)/ $a$ -SiN<sub>x</sub>:H(40 Å) multilayers is 1.8 eV, which is slightly higher than that of unlayered  $a$ -Si:H. The  $a$ -SiN<sub>x</sub>:H, used as barrier layers, has an optical gap of 3.35 eV.

Figure 1 shows the log-log plot of coplanar conductance versus bias voltage at  $27^\circ\text{C}$  for the multilayered sample showing non-Ohmic behavior above 5 V. We measured the conductance with increasing bias voltage up to 300 V, at which the multilayer was bias stressed for

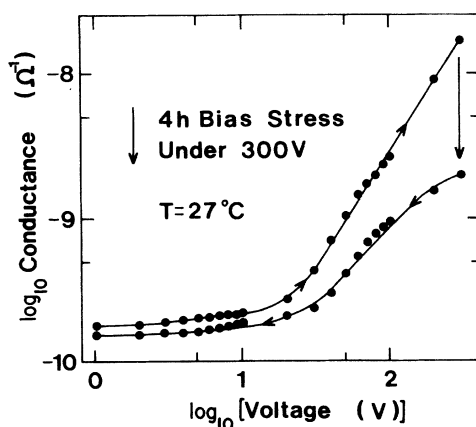


FIG. 1. The coplanar conductance vs bias voltage for the  $a$ -Si:H/ $a$ -SiN<sub>x</sub>:H multilayers at  $27^\circ\text{C}$ . The vertical arrow indicates 4-h bias stress under 300 V.

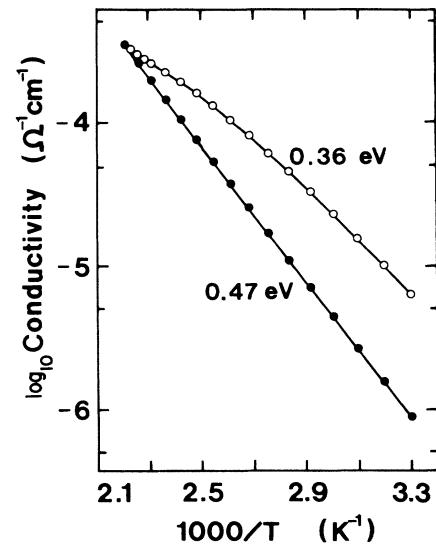


FIG. 2. Temperature dependence of conductivity for annealed and PPC states in the multilayers. The PPC was generated by 1 min of illumination with  $50\text{-mW}/\text{cm}^2$  white light at room temperature.

4 h, and then measured the conductance with decreasing bias voltage. The current is saturated to a quasisteady value in a few seconds and then decreases slowly at each bias voltage.

Figure 2 shows the temperature dependence of coplanar conductivity for the annealed and PPC states in the  $a$ -Si:H/ $a$ -SiN<sub>x</sub>:H multilayers. All conductivities reported hereafter were measured at the Ohmic region below 5 V. The PPC state was generated at room temperature by 1 min of illumination with white light of  $50 \text{ mW}/\text{cm}^2$ . The activation energy of conductivity changes from 0.47 eV (annealed state) to 0.36 eV (PPC state). The PPC starts to be annealed at  $100^\circ\text{C}$  and nearly disappears at  $180^\circ\text{C}$  with the heating rate of  $4^\circ\text{C}/\text{min}$ . It should be noted that space-charge doping raises the Fermi level by about 0.35 eV in  $a$ -Si:H well layers for the annealed state.

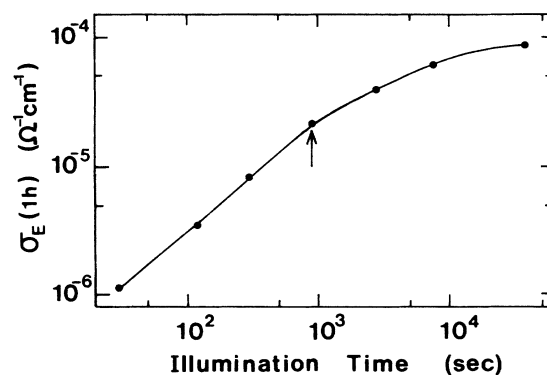


FIG. 3. Excess conductivity  $\sigma_E$  measured 1 h after turning off the light as a function of illumination time at room temperature. The arrow indicates illumination time at which  $\sigma_E$  starts to be saturated.

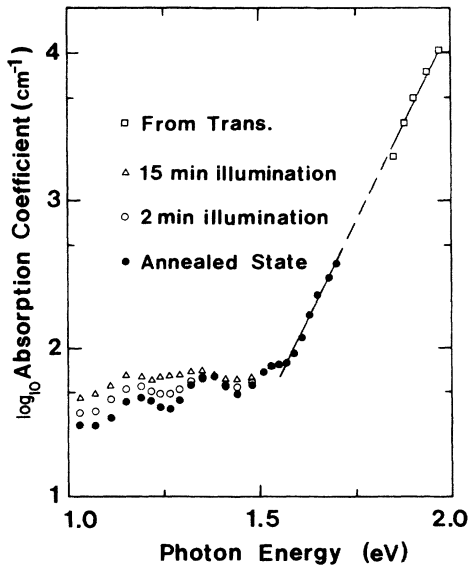


FIG. 4. Absorption coefficient vs photon energy for annealed and PPC states in the multilayers. The exponential part of the optical absorption determined by CPM is fitted to transmittance data.

This was obtained from the measurements of the temperature dependence of conductivity for both single-layer *a*-Si:H and the multilayered sample.

It is shown in Fig. 3 that the light-induced excess conductivity  $\sigma_E$  increases almost linearly with illumination time up to  $10^3$  sec, above which the  $\sigma_E$  tends to be saturated. The  $\sigma_E$  was measured 1 h after turning off the light. This saturation behavior of the PPC with illumination time is similar to that in an unlayered, compensated *a*-Si:H film doped with both phosphorus and boron.<sup>18</sup>

Figure 4 shows the sub-band-gap absorption spectra measured by the CPM for the annealed and PPC states. The exponential part of the absorption coefficient determined by the CPM was fitted to transmittance data. After a brief white-light illumination which induces the PPC in *a*-Si:H/*a*-SiN<sub>x</sub>:H multilayers, the optical absorption coefficients below a photon energy of 1.5 eV increase. Note that the sub-band-gap absorption and  $\sigma_E$  increase with illumination time at nearly the same rate up to  $10^3$  sec. The sub-band-gap absorption coefficient at 1.3 eV of a multilayered film is an order of magnitude higher than that of an unlayered intrinsic material and thus the energy regime of the exponential Urbach tail is shortened, which is attributed to the interface states between *a*-Si:H and *a*-SiN<sub>x</sub>:H.

The effects of high-temperature annealing above the deposition temperature on the PPC in the multilayers are shown in Fig. 5. Annealing was carried out at each temperature for 1 h in a vacuum of  $10^{-6}$  Torr pumped by a turbomolecular system. The data points reported here were obtained from the different samples which were prepared simultaneously by glow discharge decomposition. As the annealing temperature ( $T_A$ ) is increased, the  $\sigma_E$  decreases more rapidly than the photoconductivity

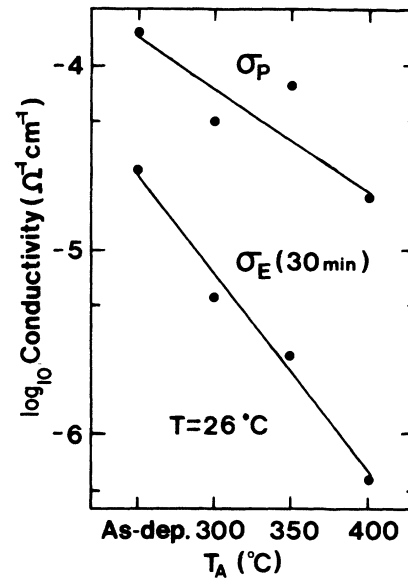


FIG. 5. Photoconductivity and excess conductivity as a function of annealing temperature  $T_A$ . Annealing was carried out at each temperature for 1 h. Excess conductivity is measured 30 min after turning off the light at 26°C. The data points are obtained from different multilayers which are prepared simultaneously in a reactor.

$\sigma_P$ . The  $\sigma_E/\sigma_A + 1$  as a function of annealing temperature is shown in Fig. 6. The PPC is reduced to a negligible value, but is still observable upon 400°C annealing.

Figure 7 shows the sub-band-gap absorption of 350°C, 1-h annealed multilayers before and after 15 min of illumination at room temperature. After 15 min of illumination inducing the PPC of  $\sigma_E/\sigma_A = 1.1$ , the sub-band-gap absorption increases slightly below a photon energy of 1.4 eV. The absorption coefficient of 350°C-annealed sample is higher than that of the as-deposited one by a factor of 2 at a photon energy of 1.2 eV.

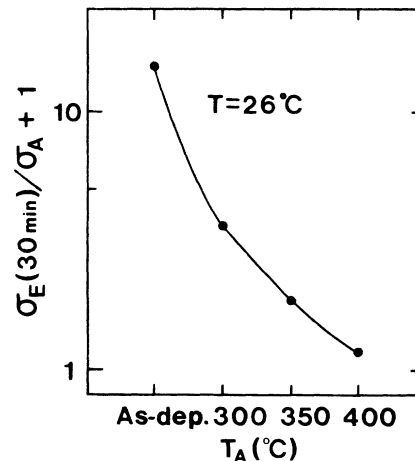


FIG. 6. The  $\sigma_E(30 \text{ min})/\sigma_A + 1$  vs annealing temperature. The data are from Fig. 5. The  $\sigma_A$  denotes the conductivity of the annealed state for each multilayered film.

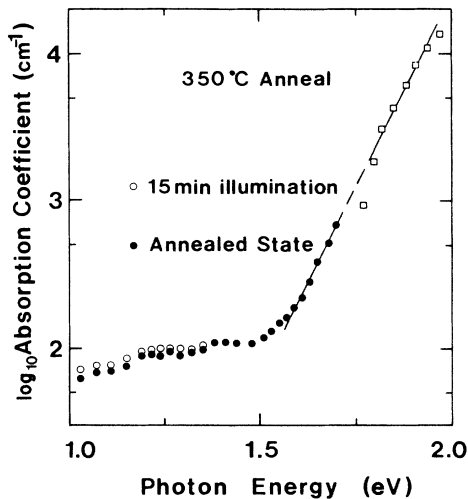


FIG. 7. Absorption coefficient vs photon energy for the annealed and PPC states after 350°C annealing for 1 h. The  $\sigma_E$  is the same as the  $\sigma_A$  at 26°C after 15 min of light illumination.

Figure 8 shows the temperature dependence of dark conductivity for the rapidly and slowly cooled states of the  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayered film. After thermal quenching from the temperature of 180°C, the coplanar conductivity increases appreciably and the Fermi level is slightly shifted toward the conduction band from 0.47 to 0.46 eV below the band edge.

Figure 9 shows the temperature dependence of conductivities for the slowly and rapidly cooled states in the unlayered intrinsic and the intentionally nitrogen (N)-contaminated  $a\text{-Si:H}$  films. Contrary to the multilayered film, the conductivity decreases upon rapid cooling in both materials. The N-contaminated  $a\text{-Si:H}$ , made using a gas mixture of  $[\text{NH}_3]/[\text{SiH}_4]=0.02$ , has the optical gap of 1.8 eV and the photoconductivity comparable to that of intrinsic  $a\text{-Si:H}$  at room temperature. It is noted that

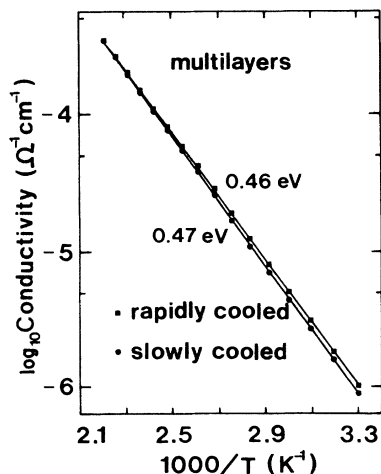


FIG. 8. Temperature dependence of conductivity for slowly and rapidly cooled states in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers.

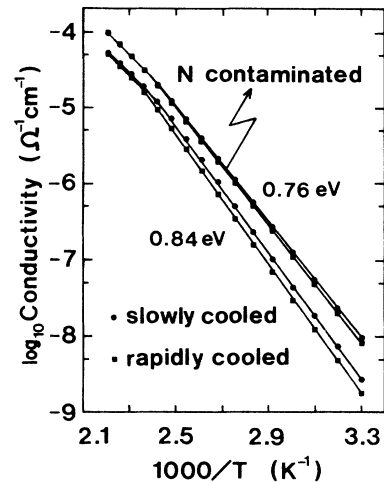


FIG. 9. Temperature dependence of conductivities for slowly and rapidly cooled states in the unlayered intrinsic and the intentionally nitrogen-contaminated  $a\text{-Si:H}$  films.

the kink in temperature dependence of conductivity appears at 150°C for both films.

The variation of dark conductivity ( $\sigma_d$ ) with time ( $t_d$ ) at 180°C after termination of light illumination is shown in Fig. 10 for the N-contaminated  $a\text{-Si:H}$ . The sample is exposed to light for 10 min at 180°C. After turning the light off, the  $\sigma_d$  drops below the value of the annealed state shown by the horizontal dashed line. But the conductivity rises rapidly with time and overshoots the annealed value in a few minutes and finally decreases slowly over a period of several hours to the annealed value. This result is consistent with that observed in lightly P-doped  $a\text{-Si:H}$  by Deng and Fritzsche.<sup>20</sup>

#### IV. DISCUSSIONS

##### A. Bias voltage-induced effect

The non-Ohmic carrier (electron) injection effect in the coplanar conductance of an  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayered film at a moderately high bias voltage is attributed to the transverse (vertical to interface) electric fields which may have arisen from the inhomogeneity of inter-

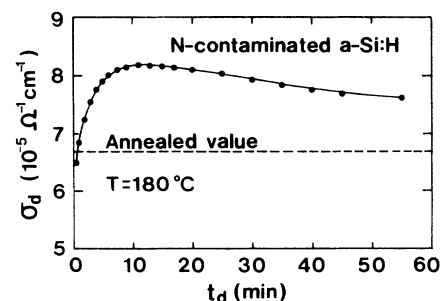


FIG. 10. Time dependence of dark conductivity at 180°C after 10 min of light illumination for the N-contaminated  $a\text{-Si:H}$ . The horizontal dashed line indicates the annealed state conductivity.

faces and/or of external electrode contacts. Ugür<sup>15</sup> has reported the bias-induced effects, which were characterized by a long time constant and enhanced conductance when the multilayer was subjected to a moderately large bias. He associated these effects with the transverse potential difference that resulted from conductance inhomogeneities in adjacent *a*-Si:H sublayers.

An electron accumulation in the well layers of *a*-Si:H creates defect states near interfaces and/or in well layers, as in an *a*-Si:H thin-film transistor (TFT). It is well known that the positive gate biasing in the *a*-Si:H TFT creates defect states at the interface between *a*-Si:H and *a*-SiN<sub>x</sub>:H.<sup>21</sup> Thus the coplanar conductance of the multilayers decreases after 300-V bias stressing even at room temperature, as shown in Fig. 1. We have reported in previous papers<sup>22,23</sup> the bias-induced changes in the coplanar and transverse conductances of an *a*-Si:H *npnp* ··· doping-modulated multilayers, in which the transverse electric field is also a crucial factor.

### B. Photoinduced effect: Persistent photoconductivity

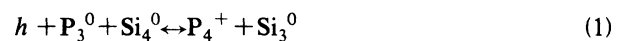
The persistent photoconductivity effect observed in our multilayered *a*-Si:H/*a*-SiN<sub>x</sub>:H samples lasts for many days at room temperature and is annealed away above 100°C, as in *n-p-n-p* ··· *a*-Si:H doping-modulated multilayers and compensated *a*-Si:H film. We can also observe a large PPC by the light illumination of 6000–8000 Å which is hardly absorbed in the barrier layers of *a*-SiN<sub>x</sub>:H. The generation of PPC is known to be thermally activated with the activation energy of around 0.30 eV.<sup>14</sup> Thus we consider that the PPC effect may not only be associated with trapping of a charge at the interfaces or in the barrier layers of *a*-SiN<sub>x</sub>:H. Agarwal and Guha<sup>12</sup> observed, for the first time, the PPC effect in *a*-Si:H/*a*-SiN<sub>x</sub>:H compositional multilayers made by the glow discharge method and explained their results in terms of deep traps at the interfaces. However, a trap model might not give rise to the long time constant of PPC at and above room temperature and to the increase in sub-band-gap absorption for the PPC state after a brief light illumination, as shown in Fig. 4. Moreover, illumination of sub-band-gap light below a photon energy of 1.2 eV does not quench the PPC and sometimes results in enhancing the PPC. Very recently, Chen *et al.*<sup>19</sup> proposed some novel defect center similar to the *AX* center<sup>24</sup> in *n-i-p-i* ··· *a*-Si:H multilayers in order to explain the PPC effect in *a*-Si:H/*a*-SiN<sub>x</sub>:H multilayers. They attributed *AX* centers to the negatively charged dangling bonds near interfaces in the multilayers. But, the *AX*-center model does not explain our experimental result of the increase in defect states (sub-band-gap absorption) upon a short illumination which is hardly intense enough to induce the Staebler-Wronski defects, as will be discussed next.

Usually, the sub-band-gap absorption spectra of an *a*-Si:H film is measured by photothermal deflection spectroscopy<sup>25</sup> (PDS) or the CPM.<sup>26</sup> The CPM measures an absorption which occurs in the transport regime of the charges, while the PDS measures that which occurs in all regimes of the sample. Using the CPM, therefore, we can

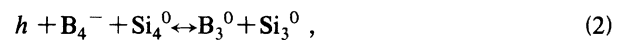
measure the gap-state absorption taking place in the *a*-Si:H well layers and/or near the interfaces rather than in the *a*-SiN<sub>x</sub>:H barrier layers of multilayers.

A prolonged illumination with intense light leads to the creation of additional metastable states in the gap of *a*-Si:H, which is referred to as the Staebler-Wronski effect.<sup>27</sup> But, the Staebler-Wronski defect is negligibly created in *a*-Si:H upon 15 min of illumination with 50 mW/cm<sup>2</sup> used in generating the PPC effect in *a*-Si:H/*a*-SiN<sub>x</sub>:H multilayers. This was confirmed by the fact that the CPM spectra of unlayered, intrinsic *a*-Si:H film made in the same reactor as the multilayers remained almost unchanged after 15 min of illumination. Therefore, after a brief light illumination, the increase in sub-band-gap absorption of the *a*-Si:H/*a*-SiN<sub>x</sub>:H multilayers implies that the metastable defect states in *a*-Si:H well layers and/or near interfaces are created. To check the effect of remnant N contamination in *a*-Si:H well layers during gas exchange, we prepared an intentionally N-contaminated *a*-Si:H film and compared the light-induced effect with the multilayers. The N-contaminated film shows the normal Staebler-Wronski effect and the negligible increase in sub-band-gap absorption upon 15 min of light illumination at room temperature. Thus we infer that the increase in defect states after a short illumination is mainly due to the creation of metastable defects near the interfaces and the PPC effect in *a*-Si:H/*a*-SiN<sub>x</sub>:H multilayers is correlated with these metastable defects generated by light.

Based on the results of hole injection for compensated *a*-Si:H, we have recently proposed that hole-induced dopant conversion and the dangling bond formation process are responsible for the PPC in the compensated film.<sup>28</sup> Injected holes are trapped in dopants or weak silicon bonds near dopants and these hole trappings cause the creation of dangling bonds as well as the conversion of dopants by the following reactions:

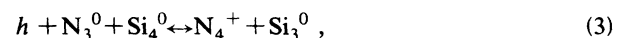


or



where *h* denotes an injected hole, the suffix of the symbols stands for the coordination number, and the prefix represents the charge state.

Similarly, we want to propose that the PPC effect in *a*-Si:H/*a*-SiN<sub>x</sub>:H multilayers is associated with the dopant activation of nitrogen at and/or near the interfaces. Accordingly, the following reaction near the interfaces is possible:



where *h* is a photoexcited hole. This reaction proceeds through the motion of hydrogen bonded to silicon near the interfaces. This model can explain the observed results that the sub-band-gap absorption increases after a brief light illumination which induces the PPC in multilayers.

Whether the substitutional nitrogen, N<sub>4</sub><sup>+</sup>, can exist in an *a*-SiN<sub>x</sub>:H is rather questionable. Recently, Shimizu

*et al.*<sup>29</sup> reported that the major charged defect in an  $a\text{-SiN}_x\text{:H}$  is  $\text{Si}_3^-$  intimately paired with  $\text{N}_4^+$ , in contrast to the model of  $\text{N}_2^-$  and  $\text{Si}_3^+$  proposed by Robertson and Powell.<sup>30</sup> We observed the shift of Fermi level toward the conduction band edge in the intentionally N-contaminated  $a\text{-Si:H}$  having moderately good electronic properties. This indicates that N incorporated into amorphous silicon film is likely to act as a donor with very poor efficiency. In laser-annealed N-implanted crystalline silicon, the substitutional N center, labeled SL5, having an axial distortion in the positions of the N and neighboring Si atoms, was observed by the electron paramagnetic resonance (EPR) experiments.<sup>31</sup>

Our model predicts that reaction (3) is possible in the bulk  $a\text{-Si:H}$  containing N under a certain environment. This behavior is shown in Fig. 10. The light illumination at an elevated temperature gives rise to excess conductivity after the recovery of the Staebler-Wronski effect. We suggest, therefore, that the metastable active donor  $\text{N}_4^+$  is generated by light illumination in the N-contaminated  $a\text{-Si:H}$  and reaction (3) is plausible. Deng and Fritzsche<sup>20</sup> observed a similar effect in P-doped  $a\text{-Si:H}$  and interpreted the increase in conductivity as the conversion of  $\text{P}_3^0$  into  $\text{P}_4^+$  accompanied by  $\text{Si}_3^-$  generation. The light-induced excess conductivity at high temperature was observed also in undoped  $a\text{-Si:H}$ ,<sup>32</sup> which might be explained by our model because N impurity as high as  $10^{17} \text{ cm}^{-3}$  is contained in an undoped sample even prepared by an ultrahigh vacuum (UHV) plasma deposition system.<sup>33</sup>

On the other hand, Maley and Lannin<sup>34</sup> have suggested from their Raman spectra on  $a\text{-Si:H/a-SiN}_x\text{:H}$  multilayers that the disorder of the bond angle increases when the sublayer thickness decreases due to the interfacial induced modifications of the network. Moreover, it was reported that the extra hydrogen of about  $10^{15} \text{ cm}^{-2}$  bonded to silicon at and near the interfaces exists when  $a\text{-Si:H}$  is deposited on  $a\text{-SiN}_x\text{:H}$ .<sup>11</sup> Under these circumstances, the configuration of N and neighboring Si atoms might be very easily changed compared with single-layered film, so that reaction (3) is likely to occur during light illumination.

Now consider the effects of high-temperature annealing above the deposition temperature on the PPC in a multilayered sample. As annealing temperature is raised, the magnitude of PPC decreases drastically, as shown in Figs. 5 and 6. This result appears to be due to the effusion of hydrogen. The hydrogen motion at and/or near the interfaces is necessary in reaction (3), describing the dopant activation of N. The out diffusion of hydrogen is inferred from the decrease in photoconductivity and the increase in sub-band-gap absorption after annealing, as shown in Figs. 5 and 7. It should be noted that the small PPC effect in the  $350^\circ\text{C}$ -annealed multilayers is in accordance with the very small increase in sub-band-gap absorption spectra for the PPC state. The results of annealing at high temperatures support our model for the PPC effect in  $a\text{-Si:H/a-SiN}_x\text{:H}$  multilayers. Choi *et al.*,<sup>35</sup> on the other hand, investigated the high-temperature annealing effect on the PPC in doping-modulated  $n\text{-p-n-p} \cdots a\text{-Si:H}$  multilayers and in com-

pensated film. The PPC is greatly quenched upon annealing in both samples, as in  $a\text{-Si:H/a-SiN}_x\text{:H}$  multilayers. The effusion of hydrogen from samples suppresses reactions (1) or (2), so the PPC disappears after high-temperature annealing.

We are forced to consider the thermal stability of a  $a\text{-Si:H/a-SiN}_x\text{:H}$  multilayered structure in the isochronal annealing experiments above the deposition temperature. Miyazaki, Ihara, and Hirose<sup>36</sup> reported that the layer spacing for the  $a\text{-Si:H}$  (25 Å)/ $a\text{-Si}_3\text{N}_4\text{:H}$  (50 Å) multilayers remained unchanged for annealing temperatures up to  $600^\circ\text{C}$ . Full width at half maximum (FWHM) for the first Bragg peak exhibits a little change after annealing at  $400^\circ\text{C}$ , while that of the higher-order diffraction peak significantly decreases by  $400^\circ\text{C}$  annealing. This, they suggested, implies that the hydrogen effusion from the multilayers improves the structural homogeneity.

### C. Thermally induced effect

The frozen-in excess conductivity parallel to the layers is observed in the multilayered film after rapid cooling from  $180^\circ\text{C}$ . Although the ratio of conductivity for the rapidly cooled state to that for the slowly cooled one is about 1.2 at  $22^\circ\text{C}$ , the magnitude of excess conductivity is large [ $\sim 10^{-7}(\Omega \text{ cm})^{-1}$ ]. This thermally induced effect in the multilayers can be explained by reaction (3). The increase in thermally excited holes and diffusivity of interfacial hydrogen at a higher temperature causes reaction (3) to proceed to the right. The left-hand side of Eq. (3) is the ground state, indicating that the density of excited  $\text{N}_4$  states increases exponentially with temperature. The thermal quenching results in excess  $\text{N}_4^+$  and a dangling bond density at room temperature. We infer that the conversion of threefold coordinated N into an active donor overwhelms the increase of dangling bond density in  $a\text{-Si:H}$  well layers when the  $a\text{-Si:H/a-SiN}_x\text{:H}$  multilayers are rapidly cooled from  $180^\circ\text{C}$  to room temperature, which is due to the difference in the annealing activation energy for  $\text{N}_4^+$  and the dangling bond. This behavior can be found in the experimental data of Fig. 10. It is accepted that thermal quenching induces the frozen-in excess dangling bonds in an undoped  $a\text{-Si:H}$ .<sup>37</sup> The thermally induced increase in conductivity, on the other hand, may be associated with space-charge transfer at high temperature. We cannot exclude this possibility.

We also examined the thermally induced effect in the intentionally N-contaminated  $a\text{-Si:H}$  film. In contrast to the multilayered sample, the conductivity of N-contaminated, unlayered  $a\text{-Si:H}$  decreases upon thermal quenching as in intrinsic  $a\text{-Si:H}$ . This indicates that the single-layered N-contaminated  $a\text{-Si:H}$  is quite different from the  $a\text{-Si:H}$  well layer in  $a\text{-Si:H/a-SiN}_x\text{:H}$  multilayers because of the hydrogen rich interfacial layers.

The equilibrium temperature ( $T_E$ ) at which a structural relaxation proceeds in a few seconds is  $180^\circ\text{C}$  or higher for  $a\text{-Si:H/a-SiN}_x\text{:H}$  multilayers. This temperature is similar to that for undoped  $a\text{-Si:H}$ , but higher than that for unlayered, doped  $a\text{-Si:H}$  with phosphorus or boron.<sup>38</sup> The  $T_E$  may be related to the diffusion coefficient in a

multilayered film. It is explicit that hydrogen motion is involved in the thermal equilibrium process.<sup>39</sup>

## V. CONCLUSIONS

We have prepared  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers by rf glow discharge decomposition and investigated various metastable effects in these multilayers. The bias-induced carrier accumulation in well layers due to a transverse electric field which may originate from the inhomogeneity of interfaces results in the creation of metastable defects near interfaces and/or in well layers even at room temperature. The sub-band-gap absorption measured by

the CPM increases after a brief light illumination upon which the Staebler-Wronski defects are hardly created. The PPC for the multilayers deposited at 250°C is greatly reduced after 400-°C annealing for 1 h. Thermal quenching increases the conductivity of the multilayers, as in doped  $a\text{-Si:H}$ . We tentatively propose that the conversion of threefold nitrogen into an active donor near the interfaces is the origin of the PPC and thermally induced effects in  $a\text{-Si:H}/a\text{-SiN}_x\text{:H}$  multilayers.

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