

METASTABLE DEFECTS IN a-SiO_x:H AND a-SiC_x:H

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ABSTRACT

Metastable defects are created in hydrogenated amorphous silicon alloys presumably by the same mechanism as in a-Si:H. We find metastable defects created in a-SiC_x:H and a-SiO_x:H by hopping injection of photocarriers from adjacent a-Si:H layers. In a-SiC_x:H the defects can be created only below T=150K, they anneal at T_E=400K. In a-SiO_x:H they are created at or below T=300K, they anneal at T_E=480K. The anneal temperature is nearly independent of the creation temperature. The defects are detected by their charge exchange with adjacent a-Si:H layers whose conductance is thereby changed.

INTRODUCTION

The conductance of a layer of hydrogenated amorphous silicon (a-Si:H) sandwiched between insulating layers depends on the charge exchange between these layers which establishes electronic equilibrium, and hence a common Fermi level E_F. Any change in the insulating layers such as a change in the number of defects near E_F affects its position and thereby the conductance of the a-Si:H layer. The planar conductance of the sandwich can therefore be used to monitor the creation and annealing of metastable defects in the insulators. Such defects can be produced by a variety of means one of which is hopping injection of photocarriers from the semiconducting a-Si:H layer. Depending on the direction of the Fermi level shift one might observe either a metastable increase or decrease in the planar conductance which persists until equilibrium is reestablished.

Very large metastable conductance increases have been observed in a-Si:H/a-SiN_x:H multilayers following an exposure to light which creates electron-hole pairs in the a-Si:H layers [1, 2]. For historical reasons this phenomenon is called persistent photoconductance or PPC [3]. Although a sandwich suffices for observing the PPC effect, it is convenient to study multilayers because the effect is largest when the a-Si:H is thin (20-30 Å). In silicon/silicon nitride multilayers the PPC effect can be excited with equal efficiency at 4.2K and 300K [2]. Equilibrium is restored by annealing at T_E=460K.

This work explores whether metastable defects can be produced in the same way in other insulating materials such as a-SiO_x:H and a-SiC_x:H. We also study the temperature dependence of the defect creation process by exposing the multilayers at different temperatures and determine the annealing temperature.

EXPERIMENTAL DETAILS

The multilayers were prepared in a 13.6 MHz glow discharge chamber. The composition of the reactant gas was changed periodically between SiH₄ containing 5 ppm B₂H₆ and a mixture containing 3 parts N₂O and 1 part SiH₄ (for the silicon oxide multilayers) or between SiH₄ and a mixture of 6 parts CH₄ and 1 part SiH₄ (for the silicon carbide multilayers). Corning 7059 sample substrates were held at 510K and covered by a shutter during the change of gases and for one minute thereafter in order to obtain abrupt compositional junctions. The conductivity was calculated using the total thickness of only the a-Si:H layers.

RESULTS

We begin with the oxide multilayers and show in Fig. 1 the conductivity in the annealed state, σ_a , during exposure to 70mW/cm^2 light, σ_p , and in the PPC state after illumination. The multilayer consisted of 20 layers of slightly boron-doped a-Si:H each 30\AA thick and 21 layers of a-SiO_x:H each 400\AA thick. The boron doping is unimportant for this discussion. The PPC effect builds up gradually with exposure time and reaches a maximum near $t_e = 1\text{h}$ as shown in Fig. 2. The subsequent decrease of σ_{ppc} arises from the fact that at larger exposure times the defect creation in the oxide begins to saturate while Staebler Wronski defects begin to become noticeable in the silicon layers. This behavior agrees closely with that of silicon-silicon nitride multilayers [1]. These results were obtained at room temperature.

We now compare measurement carried out after exposing the sample at different temperatures. Fig. 3 shows the conductivity of the annealed state and the annealing of σ_{ppc} created by 30 min. exposure to 70mW/cm^2 light ($1.8 \leq h\nu \leq 2.2\text{ eV}$) at different exposure temperatures T_e . The annealing rate was $4 \pm 1^\circ\text{C/min}$. Fig. 4 shows the time dependence of the photoconductivity during exposure. First we notice that metastable light-induced changes occur at all T_e and that the equilibration temperature for these changes is about $T_E = 480\text{K}$. The observations fall into two groups. At the two higher exposure temperatures σ_p increases with exposure time. This is commonly observed in nitride multilayers [1] and is attributed to the usual increase in σ_p with rising E_F . These higher T_e yield reasonably large positive σ_{ppc} .

At the two lower T_e , σ_p decreases with T_e . This is particularly surprising at $T_e = 4\text{K}$ because at low temperatures σ_p is interpreted to be due to photocarriers hopping down in energy through localized tail states. In single a-Si:H layers σ_p at low temperatures is found to be practically independent of E_F and insensitive to reasonable changes in defect concentration. The metastable conductivity produced at the two lower temperatures can at some T be higher or lower than σ_a of the annealed state. Before we discuss these results we show data for a silicon carbide multilayer.

This sample was made with 10 layers of a-Si:H each 25\AA thick and 11 layers of a-SiC_x:H each 175\AA thick. No PPC effect was observed until the exposure temperature was lowered to below $T_e = 150\text{K}$. Fig. 5 shows the annealing curves obtained with heating and cooling rates of about 4K/min after $t_e = 50\text{ min}$ exposures at $T_e = 100\text{K}$ and 4.2K . The equilibration temperature $T_E \sim 400\text{K}$ is significantly lower than $T_E = 480\text{K}$ for the oxide and $T_E = 460\text{K}$ for the nitride multilayers [2]. Again T_E is found to be independent of the exposure temperature. The PPC effects produced at $T_e = 100\text{K}$ and 4.2K are not the same. However, we noticed that there is

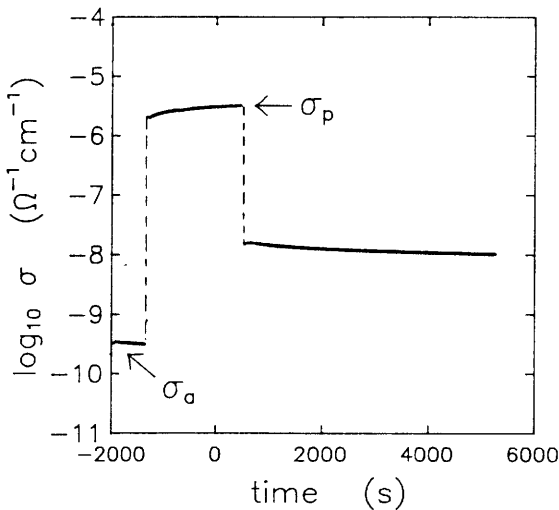


Fig. 1. Time sequence of conductivity change due to 30 min illumination. a-Si:H/a-SiO_x:H multilayer at 300K.

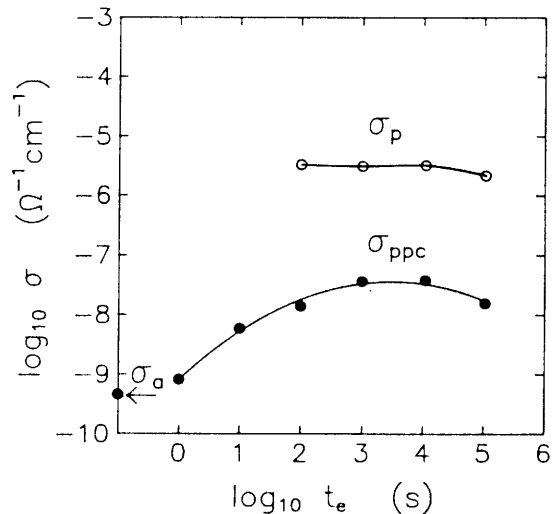


Fig. 2. Conductivity after annealing, during exposure σ_p and after exposure σ_{ppc} at 300K for oxide multilayer.

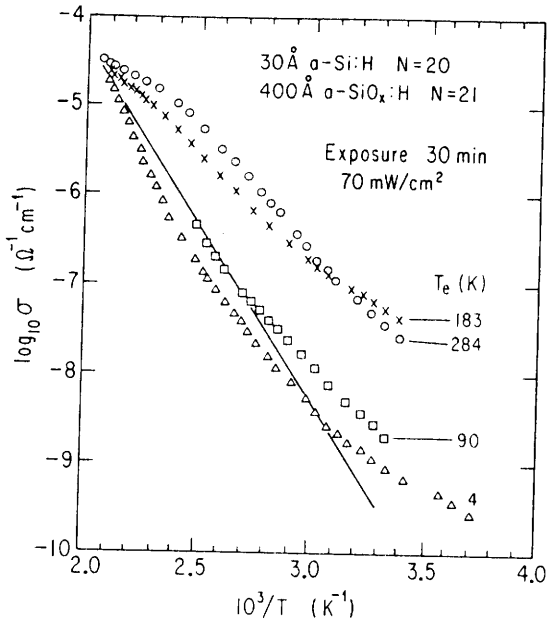


Fig. 3. Conductivity data points during heating after exposure at different T_e . Solid line is annealed state for oxide multilayer.

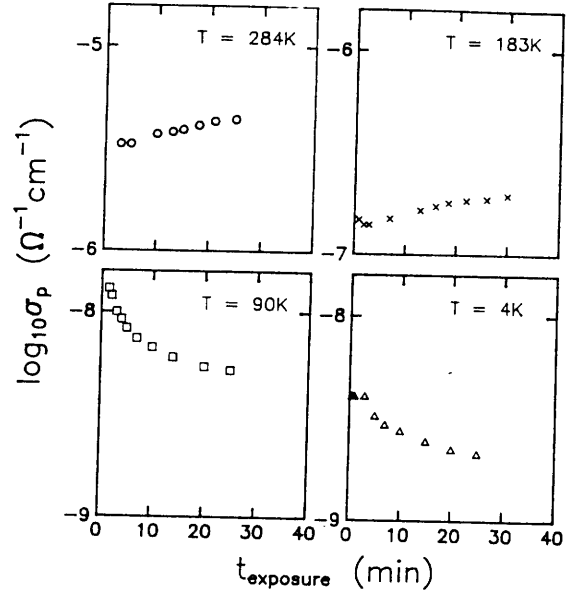


Fig. 4. Photoconductivity of oxide multilayer during exposure at different T_e .

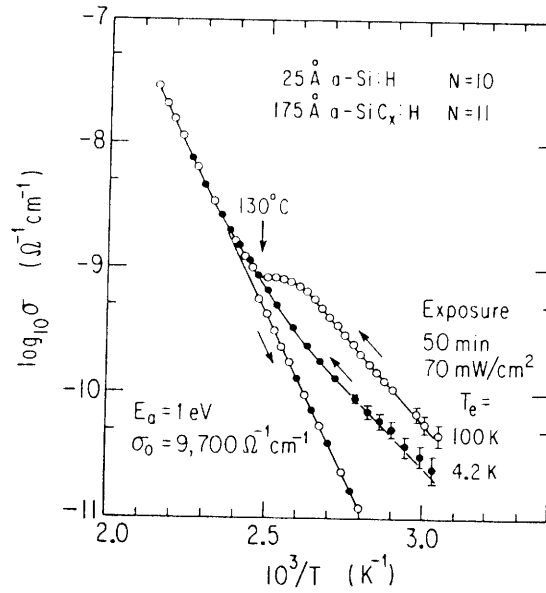


Fig. 5. Conductivity of carbide multilayer during heating after exposure at 4.2 and 100K and of annealed state.

another parameter that affects the PPC in these multilayers: high temperature annealing between 450 and 470K. With every high T annealing cycle the PPC effect diminishes and finally disappears. No such effect has been observed in the nitride and oxide multilayers. We believe that this irreversible change is due to an annealing of defects which results in a decrease in the density of localized states in the silicon carbide layers and therefore in a decrease in hopping injection from the silicon layers. This agrees with observations reported by Winer [4]. Such irreversible annealing changes are probably responsible for part of the difference in PPC induced at $T_e = 100\text{K}$ and 4.2K .

DISCUSSION

The differences in equilibration temperatures and magnitudes of the PPC effect in the nitride, oxide and carbide multilayers support our assertion that these effects are due to metastable defects produced in the insulating layers and not in the a-Si:H layers. Since the excitation light is absorbed only by the silicon layers, we conclude that these defects are caused by photocarriers hopping via localized states into the insulating layers and recombining there. T_E represents then the equilibration temperature of the insulating materials. These multilayers prove to be useful structures for studying the metastable defect dynamics in insulating materials which are difficult to excite by light directly because of their large band gap. An important result of our work is the observation that metastable defects occur generally in hydrogenated amorphous silicon alloys and that they can be produced, presumably by electron-hole recombination, even at temperatures of liquid helium. The defects probably are silicon dangling bonds.

We wish to note some interesting observations. In both the nitride and the carbide multilayers we find that the maximum temperature at which PPC can be excited lies considerably below the annealing temperature $T_e(\text{max}) = 400\text{K}$ and $T_E = 460\text{K}$ in silicon nitride and $T_e(\text{max}) = 130\text{K}$ and $T_E = 400\text{K}$ in our silicon carbide films. $T_e(\text{max})$ of the oxide films has not yet been measured. The decrease above $T_e(\text{max})$ of the efficiency of creating metastable defects may be related to our hopping injection mode of excitation.

A puzzling observation is the decrease in photoconductivity of oxide multilayers with exposure time at $T_e = 4\text{K}$ and 90K (see Fig. 4). This is not the normal decrease of σ_p with exposure which was first observed by Staebler and Wronski [5] and which is attributed to an increasing number of recombination centers. At very low T, the photocurrent is associated with photocarriers hopping down in energy through localized band tail or gap states [6]. In single a-Si:H films this has been found to be very insensitive to changes in defect concentration or position of E_F [7]. The decrease of σ_p shown in Fig. 4 appears to be connected with the layered structure of the sample and with the hopping photoconductivity as opposed to multiple trapping conduction of higher temperatures. Even though the recombination traffic is the same for electrons and for holes, their hopping rate into the insulator film can initially be different. Steady state is reached after a certain time when a potential gradient across the layers equalizes the electron and hole flows. This gradient then opposes the carriers with large hopping rate thus causing perhaps the decrease in σ_p .

The PPC observed above 270K and shown in Fig. 3 is noticeably different for low T_e (4 and 90K) and high T_e (183 and 284K) excitation. When the new defects in the oxide layers lie close to the equilibrium Fermi level one obtains a small PPC effect and σ_{ppc} can either be smaller or larger than σ_a depending on the sign of the charge transfer. We plan to use a-Si:H films with different doping concentrations in order to explore whether the present results originate from an accidental coincidence of the metastable defect energies with E_F .

The presence of PPC in silicon/insulators sandwiches or multilayers indicates not only a tendency of the insulator to form metastable defects but also a presence of localized states which permit hopping injection of photocarriers from the silicon layers. Such localized states in the insulating layers will resonate with extended states beyond the mobility edge of very thin a-Si:H layers and thus prevent the observation of sharp quantum confinement effects. Such spatial confinement effects have been observed in silicon/silicon carbide multilayers by Hattori et al. [8]. The disappearance of PPC after high T anneal of our carbide multilayers indicates that a-SiC_x:H is indeed more promising for observing the quantum confinement effects than a-SiO_x:H or a-SiN_x:H.

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