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METASTABLE DEFECT STATES AND EQUILIBRATION TEMPERATURES IN a-SiNx:H, $a\text{-}SiO_x$:H AND $a\text{-}SiC_x$:H

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Metastable defects are created by light exposure in amorphous silicon alloys at different exposure temperatures T_e. They are removed by annealing at an equilibration temperature T_E. In $a\text{-}SiN_x$:H of band gap $E_0 = 3.4$ eV the efficiency of defect creation and $T_E = 460K$ are independent of T_e between $T_e = 4$ and 300K. In $a\text{-}SiO_x$:H of band gap $E_0 = 3.3$ eV the efficiency is constant between $T_e = 4$ and 100K and then rises with T_e up to $T_e = 350K$. T_E =480K independent of T_e. In $a\text{-}SiC_x$:H defects can only be created below $T_e = 150K$, and $T_E = 400K$. Metastable defects are studied by subgap absorption and persistent photoconductivity in multilayers.

1. INTRODUCTION

Photo-induced creation of metastable defects has been obtained in several amorphous hydrogenated silicon alloys including the nitrides, oxides and carbides.[1-8] One generally finds that for small alloy concentrations the defects are Si dangling bonds. Moreover, the concentration of native defects as well as of metastable defects appears to increase with increasing band gap.[3] Some of the metastable defects produced by ultraviolet light in near stoichiometric $a\text{-}SiN_x$:H can be removed by lower energy irradiation.[4,5]

This work explores the creation by light of metastable defects and their annealing temperature in insulating hydrogenated silicon alloys having a band gap of about 3.5 eV for the oxide and nitride and 2.4 eV for the carbide. In particular we try to elucidate whether or not the creation mechanism is thermally activated. For this purpose we varied the temperature at which we carry out the light exposure between 4K and 400K.

Light excitation not only produces metastable changes of the local bonding structure but may also cause an electronic disequilibration which may result in a change in spin density and subgap absorption[5] and thus can be mistaken for a change in local bonding. These electronic metastabilities can often be bleached by subgap light. We are interested in metastable creation of new defects and not in electronic disequilibria. We try to reduce the latter by using sufficiently thin films of the insulating alloys sandwiched between more conducting a-Si:H layers so that electronic equilibrium can be established by tunneling from the alloy layers to the silicon layers.

We use two methods for detecting metastable defect changes. One is the measurement of subgap absorption of single layers by photo- deflection- spectroscopy (PDS), the other uses the metastable conductance change of a multilayer made of alternating layers of the silicon alloy and a-Si:H.[6-8] The idea of the latter method is the following. Metastable defects created in the insulating alloy or the more conducting silicon layers cause a shift of the Fermi level E_F and thus a change in parallel conductance of the multilayer. An increase in conductance must be caused by defects in the alloy layers since defects in a-Si:H shift E_F towards the gap center. The creation and annealing of such light induced excess conductance monitors therefore the creation and annealing of defect states above E_F in the alloy layers.

2. EXPERIMENTAL DETAILS

The samples were prepared at 500K in a 13.6 MHz glow discharge system. During a change of reactant gases and for one minute thereafter the substrates were covered by a shutter in order to obtain abrupt junctions. We used pure SiH_4 for a-Si:H, a $NH_3/SiH_4 = 4$ mixture for $a\text{-}SiN_x$:H, a $N_2O/SiH_4 = 3$ mixture for $a\text{-}SiO_x$:H and $CH_4/SiH_4 = 6$ for $a\text{-}SiC_x$:H. The conductivity was calculated from coplanar measurements using the total thickness of only the a-Si:H layers.

3. EXPERIMENTAL RESULTS

3.1. Oxide

The use of metastable photo-induced conductance changes of multilayers for studying metastable defect in the insulating alloy layers is based on the assumption that the changes do not result from the interfaces. We believe this assumption is valid because the effect increases with the thickness of the insulator. This is shown in Fig.1 for a series of multilayers having different oxide thicknesses and 20Å thick a-Si:H layers. For historical reasons, the increased conductance after illumination is called persistent photoconductivity σ_{ppc}.[9] Plotted here is σ_{ppc} divided by the annealed state conductivity σ_a at 300K after 20 min exposure to 100 mW/cm^2 white light. Moreover, other experiments have shown that σ_{ppc} / σ_a decreases as the silicon layer thickness is increased, hence 20-30Å thicknesses were chosen for the following studies.

Fig. 2 shows the annealing and cooling curve, measured at a rate of about 3K/min of a silicon/oxide multilayer after 30 min light exposure at different exposure temperatures T_e. Following low temperature exposures the sample was warmed to 300K within 15 min. As T_e is lowered σ_{ppc} measured at 300K decreases by an order of magnitude between T_e = 355 and 85K but then remains nearly constant to T_e = 4.2K. Regardless of T_e, the metastable defects anneal near the same temperature T_E = 480K. After exposure at T_e = 4.2 and 85K one observes in Fig. 2 some excess conductance that anneals away below 330K, perhaps a remainder of electronic equilibration.

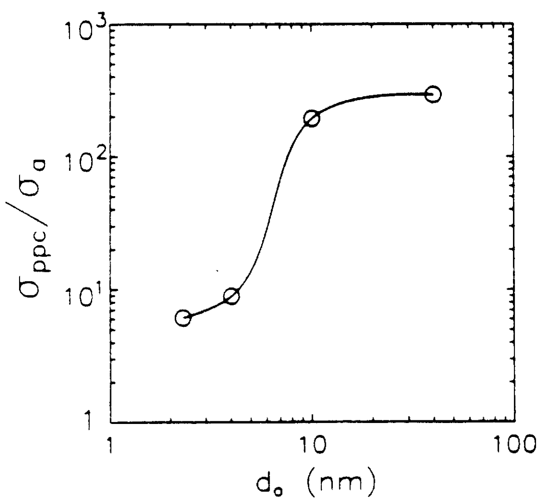

FIG. 1. Increase of persistent photoconductivity at 300K with oxide layer thickness.

Between 10 and 20 percent of the light is absorbed in the oxide layers where it may produce the metastable defects. Indeed, a metastable increase in subgap absorption is observed in 0.5μm thick oxide layers of the same composition after about 8h exposure to 100 mW/cm^2 white light from a tungsten-halogen lamp as shown in curve 2 in Fig. 2. Curves 3 and 4 were obtained after subsequent annealing for 5 min at 425K and 485K, respectively. The last anneal restored the original state curve 1. The energy gap at $\alpha = 10^4$cm^{-1} is E_{04} = 3.5 eV For comparison we show the metastable increase in subgap absorption of a typical silicon layer.

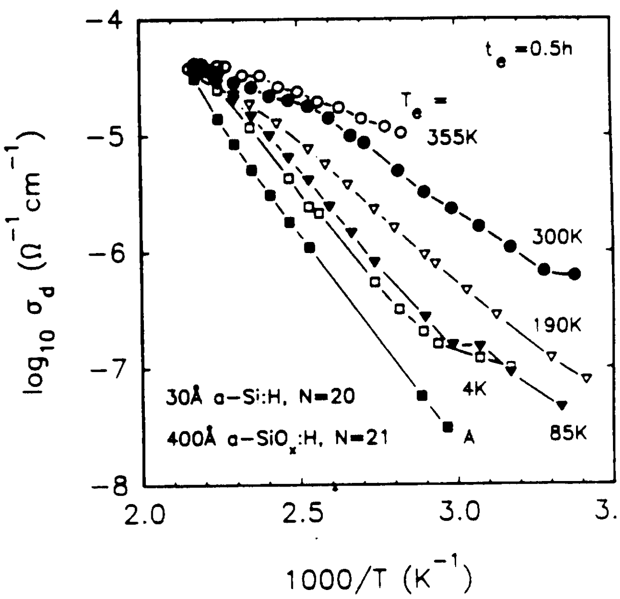

FIG. 2. Annealing curves of a-Si:H/a-SiO$_x$:H multilayer after light exposure at different temperatures T_e.

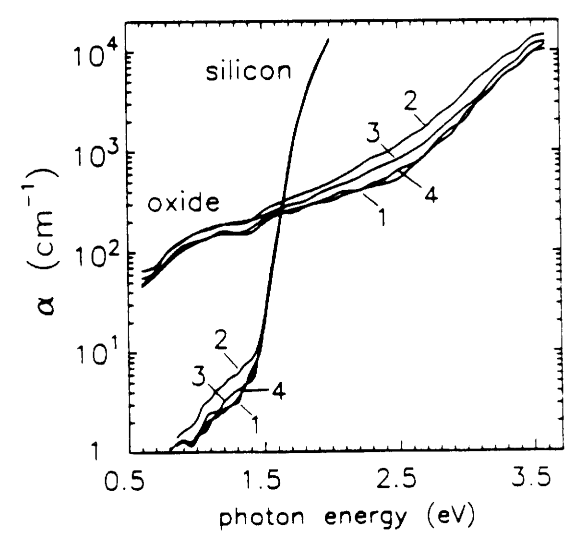

FIG. 3. Absorption coefficient α of a-Si:H and a-SiO$_x$:H layer (1) original state, (2) after 3x10^{4}s light exposure, (3) and (4) after subsequent 5 min anneal at 425 and 485K.

3.2. Nitride

We reported results on nitride multilayers earlier.[6,7] They too exhibit an increase in σ_{ppc} with nitride thickness similar to Fig. 1 and a smaller σ_{ppc} for larger silicon thickness. The nitrides are particularly interesting because the magnitude of σ_{ppc} at 300K is essentially independent of exposure temperature between T_e = 250 and 4K. σ_{ppc} begins to decrease above T_e = 300K and vanishes at 400K. Annealing curves for T_e = 4.2 and 300K are shown in Fig. 4. The equilibration temperature of the defects is T_E = 460K independent of the exposure temperature.

The subgap absorption plotted in Fig. 5 shows a metastable increase after 2.8h exposure at 300K to 100mW/cm^2 white light (curve 2) which disappears after subsequent 5 min annealing at 475K (curve 4) restoring the original state curve 1. The gap energy at $\alpha = 10^4$cm^{-1} is E_{04} = 3.3 eV.

3.3. Carbide

As briefly reported earlier[8] the silicon/silicon carbide multilayers studied showed a σ_{ppc} only after the exposure temperature was lowered below T_e = 150K. Fig. 6 shows the annealing curves after t_e = 50 min exposure to 2 ± 0.2eV light of 80 mW/cm^2 intensity at T_e = 100K and 4.2K. The equilibration temperature is T_E = 400K. The PPC effect produced at 100K and 4.2K are not the same.

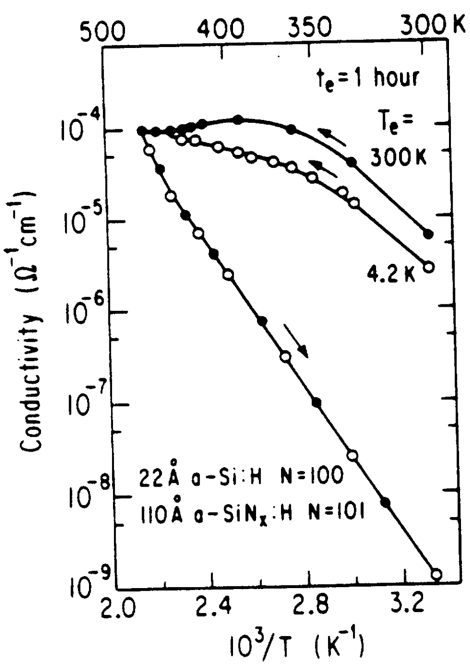

FIG. 4. Annealing of PPC state of nitride multilayers excited at 4.2 and 300K. Ref. 8.

We also noticed that after every annealing cycle to 470K the PPC diminished and finally disappears regardless of the exposure temperature. Such irreversible annealing changes are typical for silicon carbide alloys.[10]

4. Discussion

The increase of the magnitude of the PPC effect with the thickness of the insulating alloy layers as well as the differences in the equilibration temperatures in the oxide, nitride, and carbide multilayers support our assertion that these effects are due to metastable defects produced in the alloy layers and not in the a-Si:H layers.

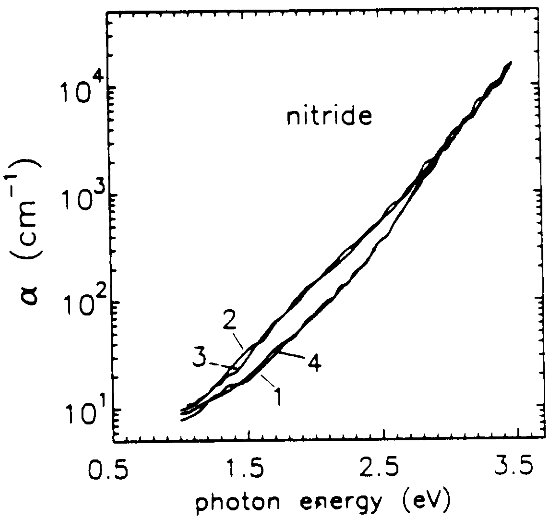

FIG. 5. Absorption coefficient α of a-SiN$_x$:H layer (1) original state, (2) after 10^5s light exposure, (3) and (4) after subsequent 5 min anneal at 425 and 475 K.

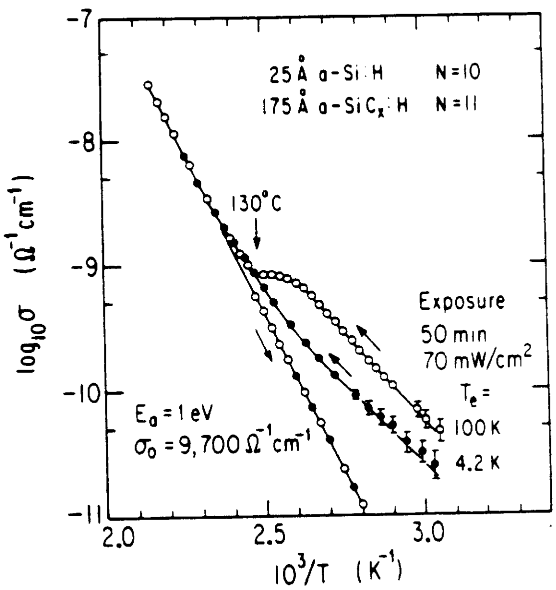

FIG. 6. Conductivity of carbide multilayer during heating after light exposure at 4.2 and 100K and of annealed state.

Previously[7,8] we proposed that the metastable defects are created in the alloy layers by photocarriers hopping via localized states into the alloy layers. Now it appears that we cannot rule out that the defects are created by light absorbed in the alloy layers. Even though only a fraction of the photons are absorbed by the alloys, these photons are remarkably efficient in creating defects in the alloys as suggested by the reversible increase in subgap absorption measured by PDS. The changes in subgap absorption reported here were produced by white light but similar results are obtained with the filtered $2 \pm 0.2eV$ light used for the PPC experiment on multilayers. At $2\,eV$, $\alpha \approx 500\, cm^{-1}$ in the oxide and only $100\, cm^{-1}$ in the nitride.

Our PPC experiments are sensitive to only those metastable defects in the alloys that lie above the equilibrium Fermi level and thus can raise it by releasing an electron. From defect absorption and ESR measurements Iqbal et. al.[11] deduced that the dangling bond defect level in a-$SiN_{1.4}$:H lies somewhat below the a-Si:H conduction band in agreement with our results. The multilayer experiments offer a convenient way for measuring the equilibration temperatures of metastable defects in the various alloys, T_E = 480K in our oxide, 460K in nitride and 400K in our carbide films. This trend reflects somehow the hydrogen content which is smallest in the oxide and largest in the carbide films. Studying a very narrow composition range Xu et al.[12] deduce the relation $T_E \approx E_0/40k$ between T_E and the optical gap E_0. Our results do not confirm this.

The highest temperature at which the metastable defects can be excited T_e (max) $\approx$ 400K for the nitride and 130K for the carbide films lie considerably below the equilibration temperatures T_E, a feature which we do not yet understand.

An important result of this work is our observation that the mechanism for photo-induced creation of defects in a-SiN_x:H is not thermally activated. Also in a-SiC_x:H as well as in doping modulated a-Si:H[13] defects are created independently of T below 100K albeit with smaller efficiency than at higher T. It should be remembered however that the efficiency of photo-induced defect creation is always very small $\approx 10^{-7}$ and that a temperature dependence can be caused by an effect of T on the competing more numerous de-excitation processes which do not yield defects.

ACKNOWLEDGEMENTS

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