Metastable states in hydrogenated amorphous carbon

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Hydrogenated amorphous carbon (a-C:H) films were fabricated by the low-frequency (60 Hz) glow discharge of the mixture of methane and hydrogen, and their electrical properties were investigated. We observed that a-C:H films show the persistent photoconductivity (PPC) by illumination of heat-filtered white light for a few seconds and the quenching-induced excess conductivity (QEC) by fast cooling from the above-preparation temperature. The PPC and QEC were about 10 times larger than the annealed dark conductivity. The samples clearly showed metastable characteristics. With increasing illumination times from 1 to 100 min, the annealing activation energy of the PPC was about 0.39 eV. The annealing temperature at which the PPC disappeared increased from 100 °C to 130 °C. Illumination longer than 80 min leads to the formation of π defects and to the decrease of PPC. From these results, we tentatively propose that the states in the π band act as deep trap centers, generating the metastabilities. [S0163-1829(96)00336-0]

I. INTRODUCTION

Until recently, hydrogenated amorphous carbon (a-C:H) films have attracted much attention as materials for optical components, mechanical and device applications.[1] It comes from the characteristics of their high thermal conductivity, optical transparency, high mechanical hardness, high electrical resistivity, large refractive index, and chemical inertness.[2–9] The structure of a-C:H films consists of mixtures of sp^2, sp^3, and even sp^1-coordinated carbon atoms in varying amounts, depending on the deposition method.

Recently, it has become known that the structural properties of a-C:H and a-Si:H are different and depend on deposition conditions. There are dangling-bond defects in a-Si:H, but there may be two kinds of defects in a-C:H.[10] As carbon may form both σ and π bonding, it is possible to have both σ and π defects in a-C:H. The π defects are expected to be easily created under an external treatment because the π bonding is weak. So, careful attention is needed to apply the models of a-Si:H to a-C:H. In spite of the differences between them, however, many of the basic properties of a-C:H, such as amorphous state, imperfect tetrahedral bonding, and the relaxation of structure by hydrogens, etc., are similar to those of a-Si:H.[11] So, we can borrow some concepts of a-Si:H to interpret the data of a-C:H.

In a previous study, we measured a metastable instability of electrical conductivity in a-C:H, prepared by low-frequency (60 Hz) plasma chemical vapor deposition (LF-PCVD), and successfully interpreted our data with a model based on the concepts of a-Si:H.[12] In the present work, we have studied the persistent photoconductivity (PPC) and quenching-induced excess conductivity (QEC) in a-C:H films prepared by LFPCVD. The PPC is a light-induced excess conductivity generated by brief illumination. It lasts several hours or days, even after termination of light at room temperature (RT). This has appeared mainly in a-Si:H-based alloys. But the detailed origin is controversial. The QEC is a thermally induced metastable phenomenon produced by fast cooling (FC) of the samples from higher than deposition temperatures. Based on our results, the possible origins of QEC and PPC will be discussed.

II. EXPERIMENTS

The a-C:H films used in this study were fabricated by LFPCVD from a mixture of methane (CH_4) and hydrogen (H_2) at RT. Corning 7059 glass substrates were used for samples for conductivity measurement, and c-silicon wafers for Fourier-transformed infrared (FTIR) spectroscopy.

The mixing ratio of methane and hydrogen gases ($CH_4/[CH_4+H_2]$) was fixed as 10 vol. %, because samples deposited in this ratio showed good electronic properties. Gas pressure during deposition was 1.5 Torr, input voltage was 250–300 V, and input current was 10–20 mA. Sample thickness ($\sim$300 nm) was measured with a profilometer (TENCOR Ins., Alpha Step 2000), optical band gap determined by UV-VIS spectroscopy (PYE UniCAM Pu 8800) was 1.9 eV, hydrogen content determined by FTIR spectroscopy (MIDAC) was about 32 at. %.[13] The relative sp^3 content ($[sp^3]/([sp^2]+[sp^3])=0.69$) was determined from relative areas under Gaussian fitting of the following bands associated with the C-H stretching modes around 3000 cm^{-1}: 3045 cm^{-1} (sp^2, aromatic), 3000 cm^{-1} (sp^2, olefinic), 2 960 cm^{-1} (sp^3, asymmetric, CH_3), 2920 cm^{-1} (sp^3, asymmetric, CH_2 and CH).[14,15] The experimental details concerning the characterization of the films have been described in a previous paper.[12]

Coplanar Al electrodes for conductivity measurements were evaporated in vacuum with 0.4-mm separation. To remove the effects of various adsorbates, and thermal, electrical and optical hysteresis, all samples were heated up over 150 °C in vacuum before measurements. We know that there are many reports on the surface-band bending in device-quality a-Si:H. But we believe that a-C:H, particularly prepared at RT, has very high density of surface state. So, we could neglect the effect of surface band bending. But in the case of applying a high electrical field, there could be a band
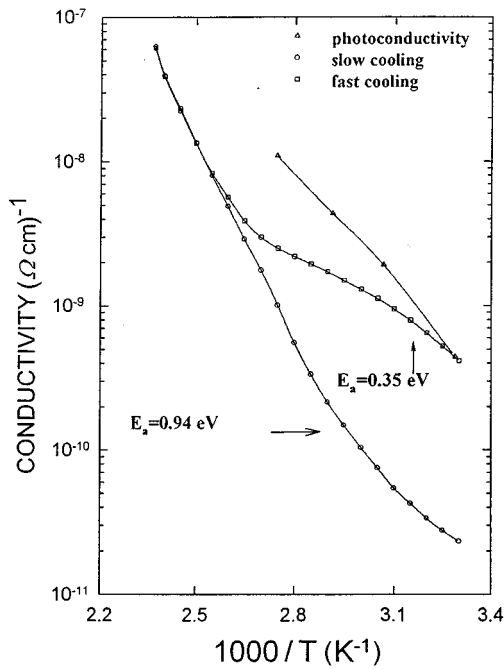
FIG. 1. The typical temperature dependence of the conductivity of a-C:H for two cooling rates from 150 °C to RT:FC; 5 °C/sec; SC, 0.025 °C/sec, and the photoconductivity generated with 50 mW/cm^2.

bending. So, we checked the linearity of the I-V curve, and applied an electric field in the linear range of the curve.[16] The conductivity was measured with Keithley 616 electrometer. Heating and cooling rates were 0.025 °C S^{-1}. For the measurements of photoconductivity and PPC, a tungsten-halogen light source with 50 mW/cm^2 was used with a heat filter (water filter).

III. RESULTS AND DISCUSSION

A. Quenching-induced excess conductivity (QEC)

The temperature-dependence of the dark conductivity as the samples are warmed-up following FC after high-temperature (150 °C) annealing for a-C:H films is shown in Fig. 1. The conductivity has been measured after FC (5 °C S^{-1}) or slow cooling (SC) (0.025 °C S^{-1}). Then the activation energy (E_a) is 0.94 eV after SC, and 0.35 eV after FC. As the films are cooled after a high-temperature annealing, two regimes of conductivity separated by a temperature T_E are observed, the low-temperature conductivity curves being merged into the high-temperature one. The temperature T_E at which the defect structure comes into equilibrium in a few minutes is about 125 °C. Above T_E, the electronic properties are independent of the prior thermal history of the film. Below T_E, conductivity is sensitive to the rate at which the film was cooled after a high-temperature annealing. The faster cooling rates give the larger dark conductivity states, a nonequilibrium state with slowly relaxing electronic and atomic structure being frozen in. Compared with undoped a-Si:H films ($T_E \simeq 190$ °C), T_E of a-C:H films is very low but similar to that of doped a-Si:H films (120 °C for n-type, 90 °C for p-type).[17] The ratio of the fast-cooled to the an-

nealed conductivity ($\sigma_{FC}/\sigma_{SC}=18$) measured at RT is larger than that (a few factor) of a-Si:H. In recent studies, it is known that T_E and σ_{FC}/σ_{SC} of undoped a-Si:H are correlated with the defect density produced by FC.[18,19] Therefore, it could be claimed that low T_E comes from the defects induced by FC. However, the induced defects may be different from that of a-Si:H because a-C:H films have the σ and π defects.

Figure 1 also shows the temperature dependence of photoconductivity (σ_p) measured during light soaking. The σ_p increased with temperature. The photosensitivity, defined as σ_p/σ_{SC}, was about 20 for a minute illumination at RT, which was much lower than that of a-Si:H ($\simeq 10^5$) and decreased with increasing temperature. It means that there is very high density of states in the gap of a-C:H, trapping the photoinduced excess carriers.

The various possible models to explain the QEC in a-Si:H include hydrogen-glass model, weak-bond–dangling-bond conversion model, etc., all of which stress a role of the dangling bonds.[18–20] It has been known that a-C:H mainly consists of two different microscopic regions, sp^3 bond and sp^2 bond regions. The sp^2 regions include π states forming π bondings. The π states of the π band are closer to the Fermi energy (E_F) than the σ states of the σ band, the π states being located near the band tail. Since the states of the sp^3 matrix are in the conduction band, it seems that most of the electrical and optical properties in the visible range are due to the sp^2 clusters.[21,22] Because π defects give a serious influence to the electronic characteristics and a-C:H films have π and σ bonds instead of dangling bonds, the metastable QEC may result from them. The results of Fig. 1 show that the density of defects in a-C:H may reach a thermal equilibrium around 120 °C. As the sample is cooled from $T \gtrsim T_E$, the relaxation time will eventually become so long that equilibration cannot be reached, and the structure is effectively frozen into nonequilibrium state. At low temperature, therefore, the electrons trapped in π states located near the band tail and defect states near Fermi-level will be slowly released, resulting in the increase of conductivity.

B. Persistent photoconductivity (PPC)

Figure 2 shows the time-dependence of the dark conductivity after illumination for 1 min at different temperatures. This is another metastability appearing in a-C:H films, the so-called PPC having a lifetime of the order of days. The PPC exhibited a fast decay at first, and then a very slow decay, lasting through measurement time. The magnitude of the PPC, defined as the ratio of the dark conductivity (σ_{PPC}) at 20 min after a 1-min illumination to the annealed dark conductivity (σ_A), ranged up to about 25 at RT. This is less than usually reported in a-Si:H.[23–25] As the illumination temperature (T_{ill}) increased, the PPC rapidly decreased. Annealing above 110 °C for 30 min completely restored the films to their original annealed states. This behavior is the same as in a-Si:H.[24,25]

Figure 3 shows the annealing behavior of PPC generated by four different illumination levels. We started to take conductivity data after PPC reached to saturation. The PPC started to be annealed at about 70 °C and completely disappeared over 120 °C. The annealing of PPC was activated in a
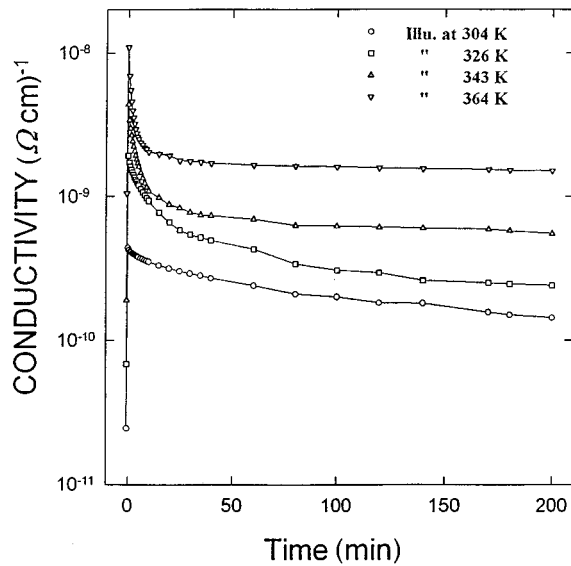
FIG. 2. The time dependence of the conductivity at various temperatures after a brief illumination at 50 mW/cm^2. After 20 min, PPC exceeds the annealed dark conductivity as much as a factor of 25.

limited temperature range and the annealing E_a was 0.39–0.42 eV, which are much smaller than 0.94 eV of the annealed state. PPC increased with illumination time, but the
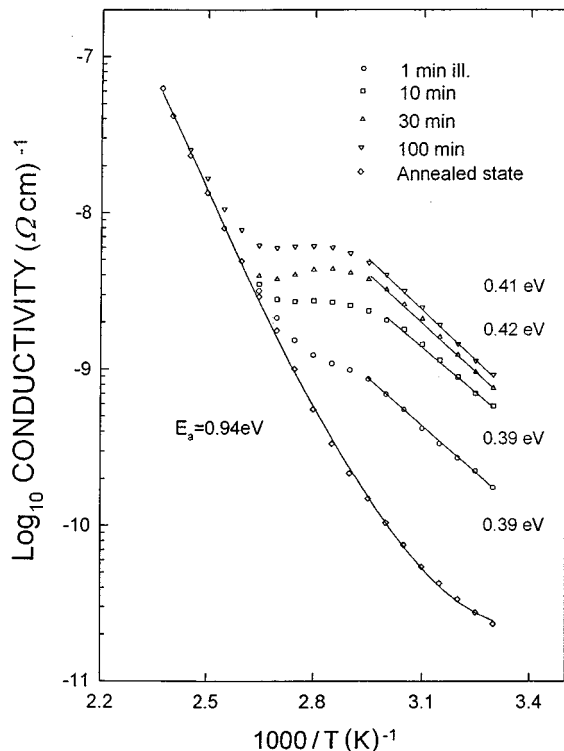

FIG. 3. The temperature dependence of conductivity for annealed and PPC states in a-C:H. The PPC states were generated by 50-mW/cm^2 white light with various illumination times at RT.
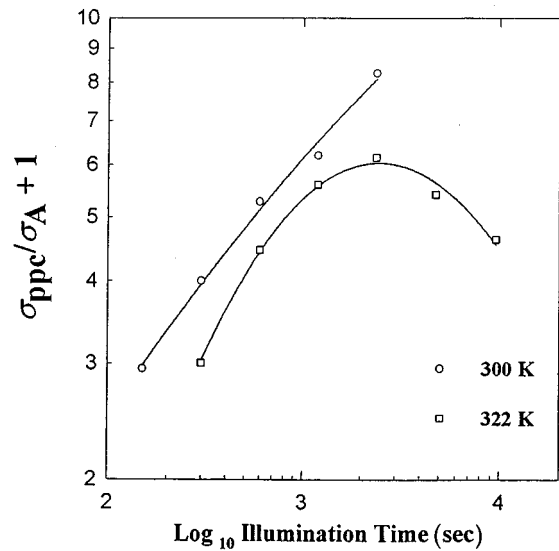

FIG. 4. Illumination time dependence of the PPC in a-C:H films. The $(\sigma_{PPC} + \sigma_A)/\sigma_A$ is the conductivity measured a half hour after the light exposure at 300 and 322 K.

annealing E_a of PPC was nearly independent of it. This behavior is the same as that of a-Si:H. Then what is the mechanism of PPC?

Recently, Hamed has studied the annealing behavior of PPC similar to the above results in their $npnp$ superlattice and compensated a-Si:H (Ref. 24) It suggested that the mobile hydrogens participate to generation and annealing of PPC. He has proposed that the annealing temperature of PPC in the Arrhenius plot may be affected by the generation of Staebler-Wronski (SW) defects with prolonged illumination, but the annealing E_a of PPC is independent of it.[24] Choi, Yoo, and Lee have also suggested the annealing behavior of PPC similar to this study.[25] Therefore, these results provide strong support that the annealing of PPC in a-C:H is closely related to the existence of the defects corresponding to the SW defects.

Figure 4 shows the normalized time dependence of PPC at 300 and 322 K as a function of illumination time. PPC was measured 30 min after illumination and was normalized by σ_A. At 300 K, PPC linearly increased with illumination time up to 40 min. On the other hand, at 322 K, PPC increased with illumination up to 10 min, and then was slowly saturated, and finally rapidly decreased. It is suggested that the decrease of PPC by prolonged illumination may be due to the generation of the defects like SW defects in a-Si:H. But the defects are not exactly the same as SW defects in a-Si:H because a-C:H has σ and π defects. The decrease of PPC by long illumination may be due to the generation of excess π defects since the π defects have smaller generation energy than the σ defects in a-C:H.

This model of defect generation can be coupled with the material hetrogeneity. Recently, Robertson have suggested the two-phase model in which a-C:H consists of sp^2-bonded planar carbon clusters embedded in a randomly oriented tetrahedrally sp^3-bonded matrix.[26] The π states form the valence- and the conduction-band-tail states in a-C:H, and consequently control the optoelectronic properties of the
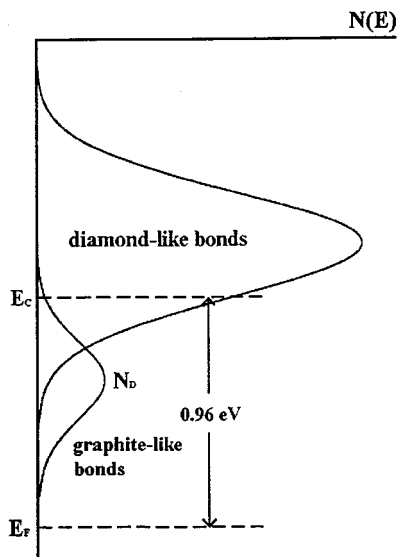
FIG. 5. Schematic band diagram of a-C:H.

material.[21,27–29] It is also suggested that the high hardness of a-C:H is correlated with the incorporated hydrogen and sp^3 sites, whereas the optical band gap is controlled by the sp^2 clusters and their various distortions.[10,30]

Figure 5 is a schematic band diagram of a-C:H showing the locations of π and σ bands.[11,31] We assumed that the π and σ bands have a Gaussian form. As shown in a previous work, the capture centers in the π band are deep states.[12] As shown in Fig. 5, π bonds are closer to E_F than σ bonds and have much smaller binding energy than σ bonds.

In order to understand our data from the above band diagram, we assumed that randomly distributed sp^2 bonds will form π bands near the σ-band tail. So, the photoinduced carriers will be trapped in sp^2 regions and are separated by potential barrier because both regions have different hydro-gen content, defect density, and optical band gap. The holes excited by illumination are captured by π states forming the valence-band tail and will be slowly released, preventing them from recombining with electrons, making the lifetime of carriers drastically long.

It has been known that PPC in a-Si:H is caused by trapping centers within the band gap.[23–25] In general, PPC is observed not in device-quality samples like an undoped a-Si:H produced by rf glow discharge of pure silane, but in low-quality samples produced by deposition of Ar-diluted silane[25] or dc glow discharge of silane.[12] It has been reported that low-quality samples with high density of midgap and tail states consist of two regions with different hydrogen content and band gaps (such as island and tissue).[33] Therefore, we propose that π states in the band tail are directly responsible for the PPC in a-C:H.

IV. SUMMARY

In this work, we report the observation of PPC and QEC in a-C:H fabricated by LFPCVD of the methane and hydrogen gas mixture. The E_a of the QEC was 0.35 eV and T_E was about 125 °C lower than that of undoped a-Si:H. With increasing illumination times from 1 to 100 min, the annealing E_a of the PPC was about 0.4 eV, and the annealing temperature at which the PPC disappeared increased over 120 °C. Illumination longer than 80 min leads to the formation of π defects and to the decrease of PPC. From the illumination time dependence of PPC and the temperature dependence of QEC, we suggest that the metastabilities observed in a-C:H were generated by deep-capture centers, possibly π defects.

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