Isomerization effect in a-Si:H

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It is well known that the hydrogenated amorphous silicon (a-Si:H) prepared from SiH₄ gas in a UHV (ultra high vacuum) system nonessentially contains carbon(C) nitrogen (N) and oxygen (O) atoms of about 10¹⁷, 10¹⁶ and 10¹⁸ cm⁻³, respectively. The electron negativity of C, N and O is 2.5, 3.0 and 3.5, respectively and these values are larger than that of Si, 1.8 and H, 2.1. Therefore, it is expected that the created Si⁺-O⁻-H⁺, Si⁺-O⁻-Si⁺ and Si⁺-H⁺ bond behave as like as ionic like bond. If a negatively (or positively) charged Si atom, T₃⁻ (or T₃⁺) exists vicinity of the H⁺(or H⁻), the H⁺(or H⁻) forms hydrogen bond with the T₃⁻ (or T₃⁺). The density of dangling bonds T₃ defects is 10¹⁴~10¹⁵ cm⁻³ in a-Si:H. These ionic like bond and hydrogen-bond make electric dipoles and that creates electronic potential and may act like as a carrier trap, a recombination center and scattering center which strongly affect carrier mobility. In this paper, especially we will discuss a trapping effect due to the ionic like bond and hydrogen bond which is with an isomerization effect of Si⁺-O⁻-Si⁺ and Si⁺-O⁻-H⁺ configurations.

Keywords: Isomerization effect, a-Si:H, Deep levels, Photo induced effect

I. INTRODUCTION

Today, hydrogenated amorphous silicon (a-Si:H) is mainly used for solar cells and thin film transistors (TFTs). The most important parameter in determining the quality of the TFTs is the carrier mobility (μ) which is affected carrier effective mass (m^*) and scattered carrier relaxation time (τ) as follows,

$$\mu = e\tau / m^* \quad (1).$$

Where e is the electron charge. There is considerable evidence for that the impurities such as oxygen (~10¹⁹ cm⁻³), nitrogen (~10¹⁸ cm⁻³) and carbon (~10¹⁸ cm⁻³) can create additional deep levels in a-Si:H which is prepared from SiH₄ gas in conventional grow discharge systems. While the prepared a-Si:H using a UHV (ultra high vacuum) system nonessentially contains carbon(C) nitrogen

(N) and oxygen (O) atoms of about 10¹⁷, 10¹⁶ and 10¹⁸ cm⁻³, respectively. ¹ However, it is observed that the O and N created only about 1 gap state for 10⁴ atoms. Therefore, recently these atoms are intentionally doped into the a-Si:H to extend a band gap.

Taylor and Ohlsen ² observed an increase in an ESR line associated with the O after light soaking a-Si:H films, and this ESR line was attributed to a hole trapped on a singly coordinated oxygen atom in a local SiO_x matrix. The deep recombination centers created by O and N reduced diffusion length in solar cells.

The electron negativity of C, N and O is 2.5, 3.0 and 3.5, respectively and these values are larger than that of Si, 1.8 and H, 2.1. Therefore, we showed an isomerization model which will be created as Si⁺-O⁻-H⁺, ³ Si⁺-O⁻-Si⁺ ^{4,5} and Si⁺-H⁺ configuration. In these

configurations, if a negatively (or positively) charged Si atom denoted as T_3^- (or T_3^+) exists vicinity of the H^+ (or H^-), the H^+ (or H^-) forms hydrogen bond with the T_3^- (or T_3^+).

Where it is known that the density of dangling bonds T_3 defects in the notation of Adler ⁶ is $10^{14}\sim 10^{15} \text{ cm}^{-3}$ in a-Si:H¹. These ionic like bond and hydrogen bond make electric dipoles and that creates electronic potential and may act like as a recombination center and scattering center which strongly affect carrier mobility.

In this paper, we will discuss that what is happen? in the isomerization effects of the $Si^+-O^--H^+$, $Si^+-O^--Si^+$ and Si^+-H^- configurations.

II. ISOMERIZATION EFFECTS

Figure 1 shows the isomerization effects, ³ which is concerned with the charging state of T_3 atoms. An $Si^+-O^--Si^+$ bond in Si crystalline makes a deep level so called A center⁷. Similarly the $Si^+-O^--H^+$ and SiOx configurations are considered to create deep levels of about $\sim 10^{15} \text{ cm}^{-3}$ because of only 1 center for the 10^4 O atoms.

In these configurations the O⁻ ions will preferentially traps a hole due to strong Coulomb force on the O⁻. The hole capture cross section of the O atom will be depended on a bond angle, θ , of the $Si^+-O^--Si^+$ and $Si^+-O^--H^+$, because these configurations have two electric dipoles moment such as M_1 , O^--Si^+ ,

and M_2 , O^--H^+ . The potential energy of M_1 and M_2 depends on the bond angle. The potential energy is as follows,

$$V \propto \frac{M_1 + M_2}{r^3} \mathbf{r} \quad (2).$$

Where r and $\mathbf{r}$ are the distance from the center of the dipoles and vector of that, respectively.

The hole capture cross section σ_p (cm^2) has both the minimum and the maximum when θ is 0° which is not real angle and the medium, 180° as shown in Fig. 2. Therefor, in DLTS (deep level transient spectroscopy) measurements, if the deep levels were measured as a constant of the capture cross section, the depth of the deep levels might be observed as distributed in the gap as shown in Fig.3 which a-Si:H was prepared using an CGD system.

Figure 1, (a) and (b) have the third dipole moment, M_3 , for $T_3^- H^+$ (hydrogen bond) and M_4 , for $O^--T_3^+$ (ionic like bond), respectively, so that the V due to the dipoles becomes weaker than that of Fig. 1, (c) and (d). The existence Fig. 1, (c) and (d) configurations is independent of that the T_3 defects exist or

Fig.1. Proposed isomerization effect in s-Si:H:O. (a) Hydrogen bond formation. (b) Ionic like bond formation. (c) Relaxed bond angle formation. (d) Relaxed bond angle formation. ³

Fig.2. Capture cross section that depended on bond angle of $Si^+-O^--H^+$ are shown in the ellipses.

Fig.3. Density of states of a-Si:H doped with boron and phosphorus at various concentrations. Measurements were DLTS.

not^{9,10,11,12} in the vicinity of the $\text{Si}^+-\text{O}^--\text{H}^+$ and the relaxed bond angle is estimated of about 104° which maybe the highest appearance probability and the deepest gap sates.

In a-Si:H which contains the O, $\sim 10^{18} \text{ cm}^{-3}$, the bulk spin density due to the T_3^0 was observed that of about $10^{14} \sim 10^{15} \text{ cm}^{-3}$. It is clear that the A centers will act as major hole trapping center rather than that of T_3^- defects that is estimated $10^{14} \sim 10^{15} \text{ cm}^{-3}$, even if the density of the A centers was $\sim 10^{15} \text{ cm}^{-3}$.

III. CARRIER TRANSPORT

Electronic transport, recombination and deep trapping in a-Si:H are determined by localized states in the gap. It is observed that electrons and holes mobility are $\mu_n \sim 2$ and $\mu_p = 4 \times 10^{-3} \text{ cm}^2/\text{Vs}$, that is, $\mu_n / \mu_p = 2000/4$ which has the O $\sim 10^{18} \text{ cm}^{-3}$. In comparison with that of crystalline Si, $\mu_n / \mu_p = 1350/480$. If the electron effective mass does not much differ from hole's one in a-Si:H, the difference of the mobility over the three order must be considered due to the difference of scattering

and trapping process, that is, the scattering for holes implies that much larger than that for electrons as mentioned above facts. Thus this phenomenon can not be explained as intrinsic effect, which the carrier scattering is mainly due to phonon, neutral defects and ionized defects.

The defect density of the ionized T_3^- and T_3^+ is almost same. A T_4^+ (Si^+) of the $\text{Si}^+-\text{O}^--\text{H}^+$ and Si^+-H^- maybe a weak ionized scattering center because it is sealed by eight valence electrons. The H^+ ($\sim 10^{18} \text{ cm}^{-3}$) is less density than that of the H^- ($\sim 10^{21} \text{ cm}^{-3}$) of the Si^+-H^- bond. Namely the deference between electron and hole mobility should not be explained by deformation scattering of phonon and Rutherford scattering of the ions. It should be considered the fact that the higher trapping centers for the hole of the O^- ($\sim 10^{18} \text{ cm}^{-3}$). Thus the big deference of the carrier mobility between two is qualitatively explained from the fact that the hole trapping centers rather than electrons one are dominant.

IV. PHOTO-INDICADE EFFECTS

Staebler and Wronski¹³ observed that prolonged light exposure causes significant changes in the dark and photo-conductivity of a-Si:H. Systematic studies have shown that changes in the dark conductivity depend on the initial Fermi level in the material as shown in Fig.4, and in slightly n-type material, the Fermi level position is pushed down toward the center of the gap and in p-type is pushed up, after light soaking. Furthermore, after a light induced, the luminescence of 0.8 eV is enhanced¹⁴ and decreased in the luminescence peak of 1.2 eV¹⁵ which is due to that between band tails.

In Fig.3 a peak of state density of about $\sim 10^{18} \text{ cm}^{-3}$ at about 0.95 eV below E_c is observed and the peak lie almost mid gap. We had discussed above that the mid gap state density was due to the A center of the $\text{Si}^+-\text{O}^--\text{H}^+$ and $\text{Si}^+-\text{O}^--\text{Si}^+$.

Under the light soaking at 200 W/cm^2 AM0 which is estimated $\sim 10^{17} \text{ 1/cm}^2\text{s}$ of photons. The strongly ionized A centers will only capture the holes such as O^- +hole and the oxygen is still negatively ionized, and then the escape time t (sec) of the captured hole is roughly calculated as,

Fig.4. Typical variations in photo conductivity and dark conductivity induced by light. ³

$$t = \frac{1}{v_t \sigma_p p_t} \quad (3).$$

Where v_t is the hole thermal velocity and p_t is the hole concentration in terms of the location of the Fermi level. Therefor A centers have a small capture cross section.

In Fig.5, the Fermi level moved toward mid-gap after light soaking and was completely recovered toward conduction band after 48 hours left in dark and air at room temperature. Now if v_t is supposed at $\sim 10^5$ cm/s, and $p_t \sim 10^{15}$ cm⁻³, σ_p is estimated $\sim 10^{-25}$ cm². This is reasonable value.

V. CONCLUSIONS

In a-Si:H, it is difficult to decrease the concentration of the O impurities below $\sim 10^{15}$ cm⁻³ in conventional glow discharge and even using UHV system so that the deep trap levels due to the A center always are considered when we discuss the electronic characteristics of a-Si:H. We have suggested an isomerization effect which explains a wide range of experimental data of the gap states in a-Si:H.

Fig.5. Typical variation in photo and dark conductivity during two hours exposure to 100mW/cm² light, two hours annealing at 150° C, two hours of re-exposure, two hours in the dark at 25° C and two days left in air in the dark at room temperature.

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