Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 243-246

Identification of Physical and Electronic Structure of Amorphous Silicon (Carbon) Hydrogen Alloy by Thermal Annealing

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The physical and electronic structure of a-SiC:H have been determined by thermal annealing experiment. Evidence shows that the mobility gap of a-SiC:H is determined mainly by the carbon concentration incorporated not in the amorphous Si-C network but in the Si-CH₃ configuration. This can be fully explained using Brodsky's quantum well model¹). The microvoid stuctures responsible for different infrared absorption peaks are also resolved. The doping and thermal annealing induced structural changes can be explained in a consistent way.

I. INTRODUCTION

The success of amorphous silicon (carbon) hydrogen alloy (a-Si(C):H) in device applications attributes very much to the large amount of hydrogen incorporated in the material, which saturate the Si dangling bonds²) and make doping possible. These hydrogen atoms (several tens at. %) would definitely play a very important role in determining the material's various properties. However, the detailed microscopic environment surrounding the Si-H (C-H) bonds and its effect on the electronic structure of the materials are still not conclusive. In this paper, by using thermal annealing such that the hydrogen atoms are driven out of the material, the above two questions can be solved by monitoring the change of the material properties.

II. EXPERIMENTS

The undoped and 1% boron and phosphorus doped a-Si:H and a-SiC:H were fabricated by RF glow discharge decomposition of silane and methane. The material properties were characterized by infrared spectroscopy (IR), optical transmission, and 17 K photoluminescence to explore its structural and optical properties. The thermal annealing experiment was conducted in a graphite boat rapid thermal annealer under hydrogen ambient.

III. RESULTS AND DISCUSSION

(A) Identification of void size surrounding SiH_X .



Fig. 1 Comparison of IR spectra for (a) undoped a-Si:H, before annealing, (b) undoped a-Si:H, after 460 °C annealing for 3 mins., (c) phosphorus doped (1%) a-Si:H, before annealing, (d) boron doped (1%) a-Si:H, before annealing, (e) boron doped a-Si:H, after 460 °C annealing for 3 mins.

Fig. 1 shows the comparison of SiH_X related IR absorption peaks of the undoped and doped a-Si:H before annealing (Fig. 1(a), (c), (d)) and undoped a-Si:H after 460 °C annealing for 3 minutes (Fig. 1(b)). It is found that the dominance of the stretching peaks changes between 2080 and 2000 cm⁻¹ depending on the doping, in addition, the 2000 cm⁻¹ peak of the undoped a-Si:H shifts to 1980 cm⁻¹ after 460 °C

annealing, which coincides with the peak position in the boron doped case. After still higher temperature annealing, no further shift of this peak is observed, which indicates that the 1980 cm⁻¹ peak is a critical one in a-Si:H. Wagner³) proposed that the 2080 cm⁻¹ peak consists of contribution from both monohydride and dihydride located on the inner surface of a "large" microvoid such that they both encounter an environment just like those on the (111) crystal Si surface on which the monohydride absorbs at 2085 $\rm cm^{-1}$. So only half of the space filled with Si medium that provides a smaller solid state screening effect. The 2000 cm⁻¹ peak is due to monohydride in a "small" void such that it is tightly surrounded by the entire dielectric Si medium. So the entire space provides the solid state screening effect. But the size of the void, i.e., how large or small need it to be a "large" or "small" void, has never been mentioned.

According to solid state effect⁴), the frequency shift of a Si-H dipole located in a cavity of radius R can be written as follows:

$$\Delta \frac{1}{\lambda} = \frac{-1}{4\pi\epsilon_0} \frac{e^{\epsilon_2}}{2\mu\omega_0 R^3} \frac{\epsilon - 1}{\epsilon + 2}$$

where ω_0 is the vibration frequency without the screening, e^* is the effective charge of the Si-H dipole, ϵ the dielectric constant of the surrounding medium, and μ the effective mass of the vibration system. If we choose R to be 1.14 Å, e^* to be 0.4 electron charge⁵, ω_0 to be 2080 cm⁻¹, $\Delta \omega$ would be 80 cm⁻¹. This value explains the frequency shift of SiH stretching mode to 2000 cm⁻¹ for those SiH monohydrides embedded in the tense Si network. Note that the dependence of the shift on cavity radius R is of power 3, i.e., if the cavity radius relaxes a little to say 2 Å, then the shift would be reduced to less than 15 cm⁻¹, and SiH can be treated as on the inner surface of a large void. As a result the peak position is strongly related to the size of the cavity in which the SiH resides.

According to the experimental fact that the absorption peak between 2000 and 2060 cm⁻¹ is never seen, and the 1980 cm⁻¹ peak appears only after the a-Si:H is annealed under high temperature. It is reasonable to conjecture that the 2000 cm⁻¹ peak is related to the smallest void in a-Si:H under normal conditions, and the next larger void will cause the 2060 cm⁻¹ peak. We propose that the so called "small" void which gives rise to the 2000 cm⁻¹ peak is the "one-Si vacancy" with four hydrogen atoms saturating the Si dangling bonds, and the so called "large" void is the "two-Si vacancy" and above, the SiH resides in "two-Si vacancy" will contribute to the 2060 cm⁻¹ peak, those in the larger void will cause absorption between 2060 to 2080 cm⁻¹. The two dimensional schematic diagram of this model is shown in Fig. 2, whereas the three dimensional diagram showing the single Si vacancy is shown in Fig. 3(a).



Fig. 2 Schematic diagram showing "one-Si vacancy" and "two-Si vacancy" in a-Si:H.

Based on this model, the change of IR spectra in Fig. 1 can be easily understood. The change of dominant stretching peak due to doping reveals that boron enhances the one-Si vacancy while phosphorus enhances the multi-Si vacancy formation. The 1980 cm⁻¹ peak of boron doped a-Si:H indicates that the cavity in which the SiH resides is an even smaller void than the one Si vacancy. Together with the fact that boron incorporates into a-Si:H mostly in SP² bonding type⁶) and significant hydrogen reduction is often observed, we propose that this small cavity is caused by a boron atom stuffed in the one Si vacancy and SP² bonds with three Si dangling bonds as shown in Fig. 3(b), the remaining SiH thus feels the shrinkage of the cavity size and absorbs at a frequency even lower than 2000 $\rm cm^{-1}$. The void structure in undoped a-Si:H causing 1980 cm⁻¹ peak after thermal annealing resembles that of the boron incorporated one Si vacancy. As the hydrogen evolves from the one Si vacancy the Si dangling bonds left behind will reconnect with other Si atom, with a little network distortion, a Si atom is stuffed in the vacancy as shown in Fig. 3(c), as a result the remaining SiH feels the shrinkage of the cavity size and the 2000 cm⁻¹ peak shifts to

1980 cm⁻¹.



- Fig. 3 Model for (a) "one-Si vacancy", (b) boron incorporated "one-Si vacancy", and (c) Si incorporated "one-Si vacancy" in a-Si:H.
 - B. Electronic structure of a-SiC:H.



Fig. 4 (a) PL, (b) IR spectra of a-SiC:H (Xg=0.8) before and after 410 °C annealing for 20 minutes.

Fig. 4 shows the PL and IR spectra of a-SiC:H (the CH₄ to SiH₄+CH₄ flow ratio Xg is 0.8) before and after 410°C annealing for 20 minutes. The PL spectrum before annealing shows a main peak at 1.63 eV with a shoulder

around 1.37 eV. This two peak structure is often observed in the PL spectrum of a-SiC:H^{7),8)}, which indicates that the material is inhomogeneous and contains at least two phases. In addition, it is found that the higher energy peak is related to C or SiC because it shifts to higher energy as more carbon is incorporated into the material. Nevertheless, the lower energy peak is not significantly perturbed by the carbon incorporation. Together with the fact that its position almost coincides with that of a-Si:H, it's reasonable to suggest that one phase in the a-SiC:H is much like the a-Si:H. After 410°C annealing the PL spectrum changes dominance from the higher energy peak to the lower one, indicating that the material at this stage is much like a-Si:H, and almost entirely loses the character of a-SiC:H. While stucturally the IR spectra shows a corresponding change around 730 cm⁻¹, which is due to the absorption of amorphous SiC network. Since thermal annealing drives the hydrogen out of the material, the remaining carbon and silicon dangling bonds reconnect to form the SiC network which causes the emerging peak at 730 cm⁻¹. Nevertheless, the loss of -CH₃ bonding (770 cm⁻¹ peak) is only 20%, which indicates that the material is still essentially a-SiC:H. It is believed that this strange behavior provides strong support to Brodsky's quantum well model. Since the carbon atom incorporates into the a-SiC:H mainly in the Si-CH₃ configuration⁹⁾, only very small amount of carbon enters into the Si network, the quantum well picture of a-SiC:H material is a natural consequence.



Fig. 5 One dimensional band diagram of a-SiC:H for (a) before (b) after annealing, showing the destruction of confinement due to SiC formation.

As shown in Fig. 5, this material is composed of two phases, one is the quantum well bounded by CH_X plus SiH_X barrier, the other is bounded by SiH_X barrier, the well region is composed of a-Si or a-SiC with very low carbon content. Due to the quantum well effect and the larger barrier height of CH_X than SiH_X , the ground state energy of the CH_X related well is higher than that in the SiHx related ones, that's the reason why the PL spectrum of a-SiC:H show double peak structure and the lower energy peak is just the characteristic of a-Si:H. After annealing the SiC is created in the CH_X barrier, which also forms a barrier but with a much smaller barrier height than that of CH_X . As a result the previously well confined carrier in the CH_X related well can now easily find a percolation path to flow into the adjacent lower energy SiH_X related wells. That's why the PL spectrum loses its a-SiC:H character and shows the a-Si:H character. The essential point of this change is that in three dimension only a small SiC opening in the CH_X barrier will completely destroy the confinement of carriers, that's why only moderate structural change is accompanied with the significant change in the PL characteristics of a-SiC:H.





According to this model, the CH_X barrier is responsible for the optical gap tailoring capability of a-SiC:H. Fig. 6 displays the relation between the optical gap E_{gopt} of a-SiC:H and the 770 cm⁻¹ peak intensity which is proportional to the $SiCH_3$ concentration. It is found that the optical gap increases monotonically with the $SiCH_3$ concentration (\circ in the figure). The reason is that as more and more CH_X barriers appears in the material, it's more and more difficult for carriers to find a percolation path to extend in the bulk, so the mobility edge is pushed higher and higher with increasing SiCH₃ concentration. As the optical absorption is mainly due to transitions in the extended states, naturally the optical gap is widened with increasing $SiCH_3$ concentration.

The role played by SiC is revealed by the odd points (•) in the figure. They represent the samples prepared under higher temperature or hydrogen dilution, the IR spectra of which show obvious SiC bonding, and give a larger R value, which is defined by the ratio of intensity between 730 and 770 cm⁻¹ peaks. It is found that the increase of SiC bonding does not widen the optical gap but rather lowers it. This is consistent with the quantum well model as the formation of SiC will destroy the confinement of carrier in the CH_X related well, the SiC opening in the barrier region makes the carrier easier to find a percolation path to become extended, the mobility gap thus shrinks and optical gap also shrinks. The implication is that the widening of the optical gap of a-SiC:H with the incorporation of carbon is not due to the alloying of carbon with Si but rather due to the large amount of CH_X barriers introduced by the carbon atoms, the introduction of SiC only reduces the optical gap.

IV. CONCLUSIONS

By thermal annealing experiment, we have determined the microvoid structure of a-Si:H. The 2080 to 2060, 2000, and 1980 cm⁻¹ peaks are caused by SiH_X in a multi-Si vacancy, monohydride in a one-Si vacancy, and monohydride in a one-Si vacancy with a boron or silicon atom stuffs in, respectively. The electronic structure of a-SiC:H is also identified to be composed of two kinds of quantum wells, the optical gap and PL peak energy are pushed to higher energy by CH_X barrier rather than the a-SiC alloy.

REFERENCES

- 1) M. H. Brodsky; Solid State Comm., 36, (1980), 55.
- G. A. N. Cornell, and J. R. Pawlik; Phys. Rev., <u>B13</u>, (1976), 787.
- H. Wagner, and W. Beyer; Solid State Comm., <u>48</u>, (1983), 585.
- 4) H. Shanks, C. J. Fang, L. Ley, M. Cardona, F. J. Demond, and S. Kalbitzer; Phys. Stat. Sol., <u>B100</u>, (1980), 43.
- 5) M. Cardona; Phys. Stat. Sol., <u>B118</u>, (1983), 463.
- S. G. Greenbaum, W. E. Carlos, and P. C. Taylor; J. Appl. Phys., <u>56</u>, (1984), 1874.
- 7) D. Engemann, R. Fischer, and J. Knecht; Appl. Phys. Lett., <u>32</u>, (1978), 567.
- 8) H. K. Tsai, W. L. Lin, W. J. Sah, and S. C. Lee; J. Appl. Phys., (1988), to be published.
- 9) W. L. Lin, H. K. Tsai, S. C. Lee, W. J. Sah, and W. J. Tzeng; Appl. Phys. Lett., <u>51</u>, (1987), 2112.