Effect of hydrogen on dangling bond in a-Si thin film

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Abstract. Concentrations of the Si-H vibration bond and the dangling bond in amorphous silicon films were studied using FTIR and ESR techniques respectively as a function of annealing temperature in the range from 20°C to 950°C. It was found that the concentration of Si-H did not change much for temperatures up to 350°C and then dropped monotonically and became negligible at temperatures above 850°C, while the concentration of SiH₂ increased with temperature and attained a maximum at 450°C and then decreased with temperature after. The ESR signal dropped with temperature, up to 200°C, and fell below the detection limit of our spectrometer in the range 200°C-500°C. The ESR signal recovered when annealing temperature was higher than 550°C. The Si-H, SiH₂, ESR and optical absorption signals were found to be highly correlated to each other and could be interpreted in a consistent manner.

1. Introduction
The role of dangling bond has a decisive effect on the properties of amorphous silicon (a-Si).[1] It has also been realized since the middle of the 70’s that the presence of hydrogen in a-Si would in many ways affect the creation and annihilation of dangling bonds. This problem has been studied extensively for decades. A well known example is the Staebler-Wronski (SW) effect [2], which involves the creation of metastable dangling bonds with midgap electronic states. A number of models [3-5] were proposed to explain the SW effect and most of them involved the interaction of hydrogen with dangling bonds, e.g. the creation of a dangling bond with the broken of a Si-H bond, the motion of hydrogen in the material through Si-H switching and the stabilization of the dangling bond, etc. The effect of hydrogen on dangling bonds is very complicated. For example, the effect of hydrogen on dangling bonds would be different in different temperature range. In this work, we tried to study in detail the change in the concentrations of the Si-H bond and the dangling bond in a-Si through thermal annealing in a wide temperature range from 20°C to 950°C. The effect of hydrogen on dangling bonds in this temperature range will also be analyzed. Samples used in this work were a-Si films produced by sputtering in an Argon gas environment with very low hydrogen concentration.

2. Methods
Samples were fabricated in an Edwards Auto 500 RF Magnetron Sputtering System with a base pressure of 3×10⁻⁶ mbar and in an Ar gas environment with working pressure of 5.5×10⁻² mbar. Both silicon wafers and quartz slides were used as substrates under each deposition condition. Source material was silicon target with 99.999% purity. Sample thickness varied from a fraction of a micron to several microns.

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Samples were annealed in a pure nitrogen gas environment at constant temperature for half an hour and all measurements were carried out at room temperature. Annealing was taken place in the temperature range from room temperature to 950°C.

The transmission spectra of the samples on silicon substrates were measured with a Perkin-Elmer FTIR system 2000 spectrometer in the mid infrared ranges at room temperature after each annealing. ESR measurements were also carried out on samples deposited on quartz substrates and after annealing under the same conditions.

3. Results and discussion

Fig. 1 shows a typical spectrum in the range of 500-1200 cm⁻¹ for an a-Si film. The dotted curve is the experimental data. The spectrum was decomposed into its component peaks using a tedious curve fitting process. The fitting parameters such as peak positions, peak widths and number of peaks were carefully considered for a large number of spectra and by making detail comparison to many known functional atomic groups. The result of the decomposition for the spectrum was also plotted in the figure, where the solid curve passing through the data was the sum of the five individual peaks. The results of those analyses showed highly systematic variations. The peaks of particular interest among the component peaks were the Si-H and the Shi₂ peaks as they were believed to be closely related to the creation and annihilation of dangling bonds in a-Si. Using the equation and the value for the cross-section area for Si-H given by Lanford and Rand [6], the concentration of Si-H in our samples was estimated to be of the order of 10¹⁸ cm⁻³, which is typical for intrinsic a-Si prepared by sputtering.

![Typical infrared absorption peaks due to impurity atoms in a-Si.](image)

The dotted curve represented the experimental data and the solid curve passing through the data is the sum of the individual peaks.

The areas of the hydrogen related peaks were calculated and monitored as a function of annealing temperatures starting from 50°C and up to 950°C. The duration of annealing at each temperature was half an hour and then cooled down to room temperature to make FTIR measurement. It was found that the area of the Si-H wagging mode started to drop significantly from 350°C and became insignificant for temperature above 850°C, as can be seen in Fig. 2 below. The variation of the peak area of Shi₂ was more complicated as it rose with annealing temperature first and attained a maximum at 450°C and then decreased with annealing temperature there after. The Si-H stretching mode had similar behavior to the wagging mode except that the drop in peak area started slightly earlier.
As the peak area of Si-H is directly proportional to the concentration of the Si-H bond, the result suggested that significant bond breaking process took place in the temperature range 350°C to 850°C. The breaking of Si-H bonds would lead to the creation of dangling bonds in a-Si with corresponding recombination centers near the middle of the energy gap. The result suggested that the concentration of the recombination center would increase with temperature in that temperature range and thus would affect the absorbance of the material accordingly. We had measured the band to band optical absorbance for the same sample and found that there was indeed a strong correlation between the optical absorbance and the Si-H concentration. The result was reported in a previous paper [7]. This led us to study the density of the dangling bonds, by means of the ESR technique, in the material in the temperature range.

The concentration of dangling bonds estimated from the ESR measurement was plotted in figure 3 using solid square symbols. The result can be divided into four regimes in temperature: (I) from room temperature to 200°C, the number of dangling bonds dropped from $10^{18}$/cm$^3$ to below the detection limit of our ESR spectrometer; (II) from 200°C to 500°C, no ESR signal could be detected; (III) from 500°C to 850°C, the concentration of dangling bonds increased significantly with temperature; and (IV) from 850°C upwards, the concentration of dangling bonds dropped. The change in Si-H concentration of the same sample was also plotted for comparison using solid triangular symbols.
Special features of Fig. 3 are summarized as follow:

1. For annealing temperature \( T_a \) from room temperature to 200°C, the concentration of dangling bonds dropped significantly while the concentration of Si-H remained fairly constant. There was no bond breaking of Si-H, as suggested by the fairly constant in the Si-H concentration. However, the hydrogen atom could move in the material, for example in the form of bond switching. Previous experimental results indicate that the diffusion of hydrogen atoms would clean up the dangling bonds.

2. For \( T_a \) from 200°C to 500°C, the concentration of dangling bonds remained in a very low level while the concentration of Si-H first decreased slightly and then dropped significantly. We believed that the bond breaking of Si-H was not significant and thus no dangling bond was created. The decrease in Si-H concentration was the reason for the increase in the SiH\(_2\) concentration.

3. For \( T_a \) in the range of 500°C to 750°C, the concentration of Si-H dropped significantly with a corresponding increase in the concentration of dangling bonds. The probability of bond breaking of Si-H increased exponentially, accompanied with the creation of dangling bonds.

4. For \( T_a \) higher than 750°C, both concentrations of Si-H and dangling bonds dropped. In this regime, crystallization also took place and the situation was much more complicated.

4. Conclusion
The results of FTIR, optical absorption and ESR on a-Si could be analyzed consistently. The concentration of dangling bonds was found to be closely related the hydrogen atoms in a-Si. At temperatures below 500°C, the bond breaking process of Si-H was not significant. The diffusion of hydrogen through Si-H bond switching eliminated the dangling bond in the material in this temperature range. For temperatures higher than 500°C the bond breaking of Si-H was important, which resulted in the creation of dangling bonds.

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