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## LIMITATIONS IN THE USE OF IR SPECTRA FOR THE DETERMINATION OF HYDROGEN CONCENTRATION IN a-Si: H FILMS

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**ABSTRACT:** Infra-red (IR) spectroscopy has been used to monitor hydrogen concentrations in hydrogenated amorphous silicon thin films. Wagging and stretching modes were used with appropriate correction factors for film thickness and proportionality constants to convert between integrated absorption and hydrogen concentration. Two different types of IR spectra were observed even though in other respects the films appeared to be identical. The values of hydrogen concentration were calculated from wagging and stretching modes. These values are in agreement for one type of IR spectrum but are not the same for the other type. Possible reasons for observed differences are presented as well as a suggestion for an improved procedure which can give more reliable values of the hydrogen concentration.

**Keywords:** Hydrogen concentration - 1: Characterisation of a-Si: H films - 2: IR - spectroscopy of a-Si: H films - 3

### INTRODUCTION

Infra-red spectroscopy is the most commonly used method for measuring the hydrogen concentration ( $C_H$ ) in hydrogenated amorphous silicon (a-Si: H) thin films since it is nondestructive, relatively fast and convenient. Additionally it can also provide information regarding the bonding configurations in the film. Most hydrogen concentration measurements are done using the method of Brodsky, Cardona and Cuomo (BCC method) [1] and rely on the measurements of the absorption intensity of the wagging mode (max. at  $635 \text{ cm}^{-1}$ ). Some researchers have tried to use the IR stretching modes (e.g. Saraie et al. [2]). This method is more complicated as two distinct stretching subbands (modes at  $2000 \text{ cm}^{-1}$  and  $2100 \text{ cm}^{-1}$ ) are observed.

Several years ago detailed investigation and evaluation of the use of both modes were reported by Maley [3] and Langford and colleagues [4]. They determined better proportionality constants between integrated absorption and hydrogen concentration for the stretching and wagging modes. In the meantime the correction factors for film thickness have been calculated and introduced in practice [5] giving more accurate values of hydrogen concentration from the IR method. It is to be expected that the hydrogen concentration determined from stretching and wagging modes ought to give the same results within an accuracy of a few percent.

### EXPERIMENTAL

In our laboratory a-Si: H thin films have been deposited using the plasma enhanced chemical vapor deposition (PECVD) method. IR spectra were collected using two different fourier transform infra-red (FTIR) spectrometers (Perkin - Elmer and Nicolet). Hydrogen concentrations were measured using both stretching and wagging modes.

Proportionality constants between integrated absorptions and hydrogen concentrations used in the calculations were taken from Maley [3] and Langford et al [4]. Correction factors for film thicknesses were taken also from Maley [3] and Maley and Szafranek [5]. Stretching modes were divided into two separated submodes at  $2000 \text{ cm}^{-1}$  and  $2100 \text{ cm}^{-1}$  using software developed in our laboratory and separate values for the proportionality constants were applied to these.

### RESULTS AND DISCUSSION

Our amorphous silicon films, although deposited under nominally identical conditions, have produced two distinctly different types of IR spectra. Figures 1, 2 and 3 represent those two typical types of IR spectra for the full scale region as well as just the regions for the wagging and stretching modes.

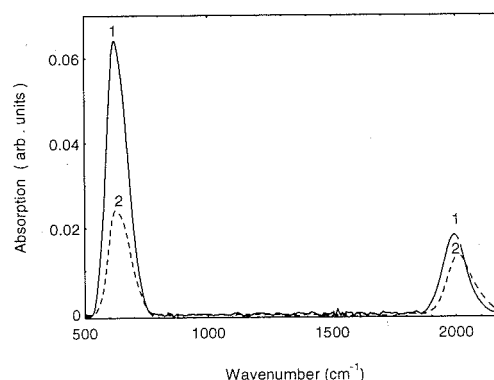


Figure 1: Infra red absorption spectra of two different types of a-Si:H films.

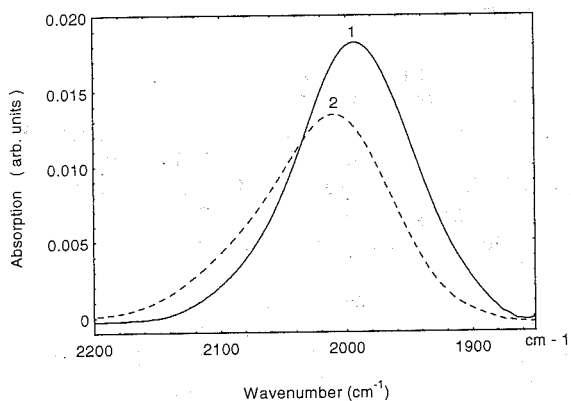


Figure 2: Infra-red absorption spectra in the stretching mode region for two different types of a-Si:H films.

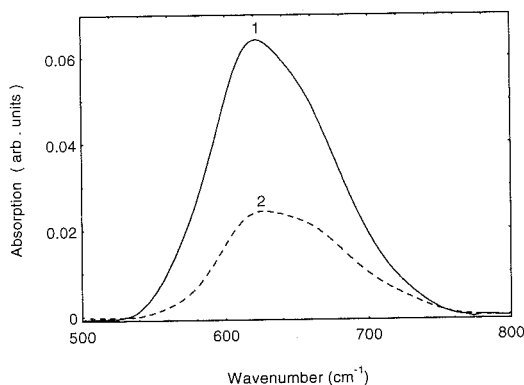


Figure 3: Infra-red absorption spectra in the wagging mode region for two different types of a-Si:H films.

Curve 1 represents the first type of sample where the intensity of the wagging mode is much higher than the intensity of the stretching mode (see Fig 1). In this case the intensity of the  $2100\text{ cm}^{-1}$  mode is quite low. Curve 2 represents the second type of sample for which the intensity of the wagging mode is only slightly higher than the intensity of the stretching mode. The intensity of the  $2100\text{ cm}^{-1}$  stretching mode is in contrast clearly higher than in sample 1.

**Table 1:** Hydrogen content of a - Si : H films calculated from the absorption of wagging and stretching modes (atomic percent  $\pm 2$ )

	Wagging mode	Stretching mode
Film 1	16	14
Film 2	9	14

Table 1 represents the results of hydrogen concentration calculations for both types of samples. For the first type of sample we obtained practically the same hydrogen concentrations using both the stretching and wagging modes. However, for the second type of sample we obtain different hydrogen concentrations for the different IR modes, where the wagging mode gave a lower value than the stretching mode. In both cases appropriate proportionality constants for  $2000\text{ cm}^{-1}$  and  $2100\text{ cm}^{-1}$  modes have been applied. This is different to what was observed by Maley [3] and Langford et al [4] who reported that the wagging and stretching modes gave the same hydrogen concentrations within 10%.

All of our films were deposited under nominally identical conditions and there is therefore no apparent reason for such substantial differences in the IR spectra and hydrogen content in the films measured. There are some possible causes of the variation in the IR spectra:

- different contributions of microcrystalline structure, microcrystalline grains or other structural components
- different bonding structures can exist in the films causing different proportionality coefficients (different oscillator strength) between integrated absorption and hydrogen concentration
- the transition probabilities for the IR wagging mode may vary
- a difference in the concentrations of the higher hydrates ( $\text{CH}_2$ ,  $\text{CH}_3$ ,  $(\text{CH}_2)_n$ ) may cause some other differences in the IR spectrum.

The discrepancies in the absorption of the wagging mode can be accounted for by molecular hydrogen, supposing that it provides a significant fraction of the total hydrogen. This was suggested for example by Shanks et al. [6], although Langford et al. [4] disagree with this possibility. Another possible explanation for the difference in the absorptions of the wagging and stretching modes is suggested by the work of Oguz et al. [7]. They found that their films contained a large amount of IR inactive hydrogen. However it is not clear how this type of hydrogen would affect just the absorption in the wagging mode.

The most distinctive difference observed between the spectra from the two samples is the shape of the stretching mode. It is easy to see that there is a higher contribution from the  $2100\text{ cm}^{-1}$  stretching component in film type 2. It remains an open question whether higher  $\text{SiH}_2$  and  $\text{SiH}_3$  concentrations are responsible for the apparent reduction in the intensity of the wagging mode, with respect to the stretching mode, in the spectrum. Further studies using other techniques such as thermal desorption are needed to provide more understanding of the material characteristics of the two films that lead to the differences in the IR spectra.

## CONCLUSIONS

From our measurements of the two apparently different types of a-Si:H films it is clear that there can still be some difficulties in using both the wagging and stretching IR modes for monitoring hydrogen concentrations. The most interesting factor is that the use of wagging mode, which has been the most popular technique used for many years, does not give consistent results

Our experience suggests the following procedure for monitoring the hydrogen concentration using IR spectra:

- use both wagging and stretching modes simultaneously with appropriate proportionality constants for the stretching submodes
- compare results obtained from both modes to avoid the situation where the second type of film will give lower values of  $C_H$
- check by another independent method (e.g. nuclear-reaction analysis, hydrogen evolution or nuclear elastic scattering) which can provide a point of reference for quantitative accuracy.

Intensive studies of other material characteristics of our films are in progress in order to provide more information and an explanation of the observed discrepancies and in particular why films prepared under nominally identical deposition conditions produce such different infra-red spectra.

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