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Characterization of plasma beam deposited amorphous hydrogenated silicon

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Fourier transform infrared spectrometry, visual transmission spectroscopy, and *in situ* ellipsometry have been performed on plasma beam deposited (PBD) amorphous hydrogenated silicon layers. From these measurements refractive index at infrared wavelengths and at 632.8 nm, the optical band gap and the hydrogen content of the layers have been determined. The hydrogen concentration of the layers varies between ~ 9 and 25 at. %. It was found that the refractive index decreases more with hydrogen concentration in the layer than predicted by theoretical calculations assuming tetrahedral structures. The band gap of the material remains constant at ~ 1.72 eV for the range of hydrogen contents measured. The resonance frequency of the SiH stretching mode (around 2000 cm^{-1}) increases with increased hydrogen content. This is additional evidence to support the assumption that clustered SiH (SiH on voids) does not have its stretching mode near the 2100 cm^{-1} SiH₂ peak. From the results presented it is concluded that PBD layers show behavior similar to plasma enhanced chemical vapor deposition layers with respect to the hydrogen content in the layers. © 1995 American Institute of Physics.

Amorphous silicon layers have been deposited using an expanding plasma beam.¹ The setup consists of a flowing subatmospheric thermal arc where an argon–hydrogen plasma is created ($n_e \cong 10^{22}\text{ m}^{-3}$, $T_e \cong 1\text{ eV}$). This plasma is allowed to expand supersonically into a vacuum vessel ($p=0.2\text{ mbar}$). Just behind the expansion nozzle of the plasma source, silane is injected into the expanding plasma beam. Under the conditions used for the *a*-Si:H deposition, the dominant radicalization mechanism is believed to be the hydrogen abstraction reaction of silane



In a silane deficient gas mixture abstraction of SiH₃ also can occur. The dissociated and/or ionized silane is deposited on a crystalline silicon and a glass substrate each of $2.5 \times 2.5\text{ cm}^2$ area. Downstream plasma parameters are typically $n_e \cong 10^{17}\text{ m}^{-3}$ and $T_e \cong 0.2\text{ eV}$, at an arc current of 50 A, argon flow of 55 scc/s, hydrogen flow of 10 scc/s, and a silane flow of 6 scc/s. Main characteristics of the set-up are a large radical flux of SiH_x and H of up to $10^{22}\text{ m}^{-2}\text{ s}^{-1}$ and $10^{23}\text{ m}^{-2}\text{ s}^{-1}$, respectively, and a low ion energy ($< 2\text{ eV}$). A similar set up is used successfully for fast deposition of *a*-C:H, diamond, and graphite.²

During deposition *in situ* ellipsometry is performed to determine the refractive index at 632.8 nm and the growth rate. From the full matrix of process conditions, the particular setting was chosen that yielded maximum refractive index at this wavelength; later the H₂ flow is varied around the optimum. Layers of $\sim 500\text{ nm}$ thickness are grown at an average rate of 15 nm/s. After deposition the layers are analyzed using Fourier transform infrared spectrometry (FTIR) to determine refractive indices at infrared wavelengths, hydrogen concentration (from the 640 cm^{-1} wagging mode),

and the concentrations of hydrogen in the SiH and SiH₂ configurations. Also the optical band gap is determined by transmission spectroscopy in the visible spectrum between 1 and 3 eV.

Typical FTIR spectra in the regions around 640 and $2000\text{--}2100\text{ cm}^{-1}$ are shown with their respective fits in Figs. 1(a) and 1(b). The values for the FWHM of the 2000 and 2100 cm^{-1} stretching modes were for the samples analyzed in the range $100\text{--}125\text{ cm}^{-1}$ and did not vary systematically with the hydrogen content in the layers. The infrared spectrum features interference fringes due to multiple reflection within the amorphous layer. As the *c*-Si substrate is single side polished coherent reflection within the substrate can be neglected. The transmission through a bare substrate is used as a reference spectrum. Analysis performed on the transmission spectrum is similar to the method used by Langford *et al.*³ The refractive index of *c*-Si is taken to be 3.42. Furthermore the (real part of the) refractive index of *a*-Si:H is taken constant over the measured range of $400\text{--}4000\text{ cm}^{-1}$. A Gaussian is chosen for the extinction coefficient (imaginary part of the refractive index) around the resonance frequencies for the different modes, and the measured transmission spectrum is fitted to an analytical expression which includes the multiple reflections. Integrating the extinction and multiplying with the correct proportionality constants yields the total concentration of hydrogen and the amounts of hydrogen in the SiH and SiH₂ configurations. The constants proposed by Langford *et al.*³ have been used to determine the absolute concentrations ($A_{640} = 2.1 \times 10^{19}\text{ cm}^{-2}$ for the total hydrogen content, $A_{2000} = 9.0 \times 10^{19}\text{ cm}^{-2}$ for SiH and $A_{2100} = 2.2 \times 10^{20}\text{ cm}^{-2}$ for SiH₂). Using an assumed density of *a*-Si:H of $5 \times 10^{22}\text{ m}^{-3}$, the determined hydrogen concentration can be converted to a hydrogen percentage.

Figure 2 shows the dependence of refractive indices at a HeNe wavelength (from ellipsometry) and at infrared wave-

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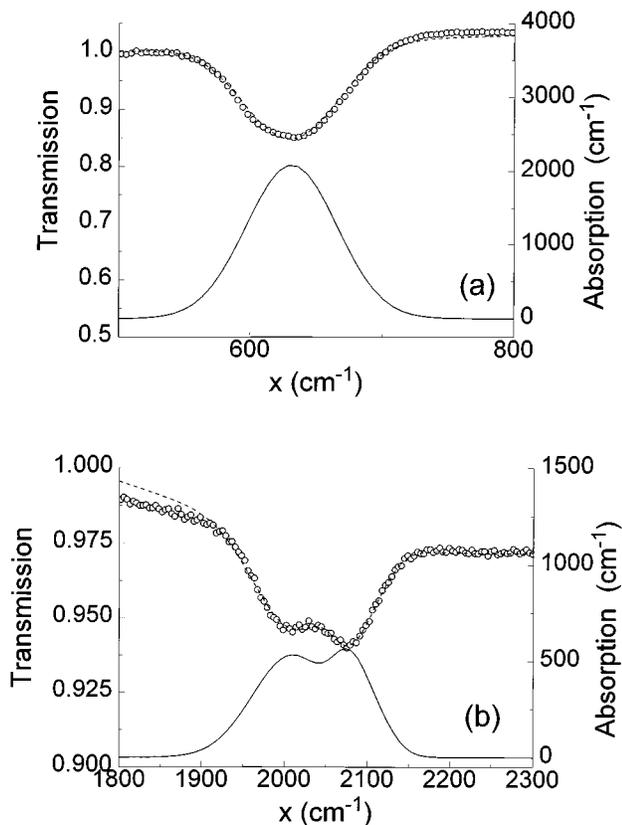


FIG. 1. Two typical FTIR spectra of PBD grown *a*-SiH in the (a) 640 cm^{-1} and (b) 2000–2100 cm^{-1} region. Dashed line—least mean square fit of the measurements; solid line—the corresponding absorption.

lengths (from FTIR) on total hydrogen concentration. The dashed line is the expected decrease in refractive index using an effective medium approximation, if the layer is assumed to consist of closely packed tetrahedral structures.⁴ In such a layer a hydrogen atom would occupy 0.45 times the volume occupied by a silicon atom. The refractive indices of the plasma beam deposited (PBD) layers decrease considerably

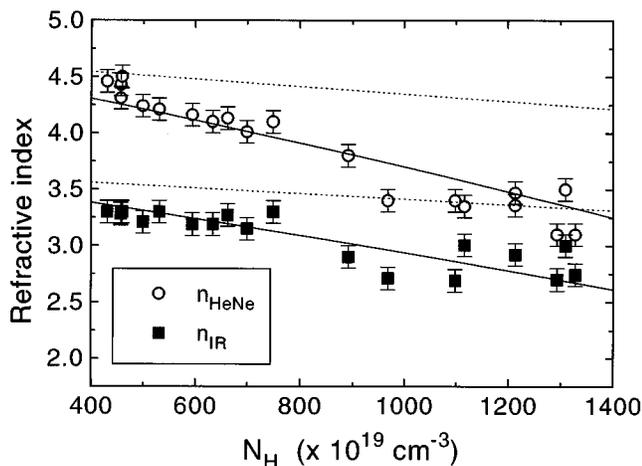


FIG. 2. Refractive indices from ellipsometry and from FTIR as a function of total hydrogen content. Dashed lines indicate the theoretical decrease assuming tetrahedral structures. The solid lines are shown as a guide to the eye.

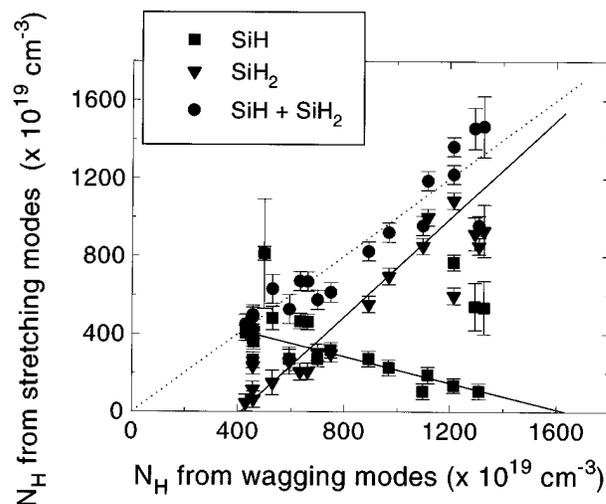


FIG. 3. Hydrogen content in the stretching modes as a function of hydrogen content in the wagging modes.

more with increased hydrogen concentration. Very similar results have been reported recently for plasma enhanced chemical vapor deposition (PECVD) layers by Daey Ouwens *et al.*⁵ The optical band gap is found to remain constant for hydrogen concentrations between 400 and $1300 \times 10^{19} \text{cm}^{-3}$. This is in agreement with measurements by Meiling⁶ on PECVD layers.

The stretching modes of SiH and SiH₂ are located around 2000 and 2100 cm^{-1} , respectively. By integrating these peaks the amount of hydrogen bonded in the SiH and SiH₂ configurations can be determined separately. In Fig. 3 the hydrogen content divided into the two configurations at 2000 and 2100 cm^{-1} , and the sum of the two is given as a function of the total hydrogen content as determined from the 640 cm^{-1} wagging modes. In the determination of the hydrogen content of the 2100 cm^{-1} mode, we took the oscillator strength for the SiH₂ stretching mode. As can be seen a good match is observed between the hydrogen content calculated from the wagging modes and the total hydrogen con-

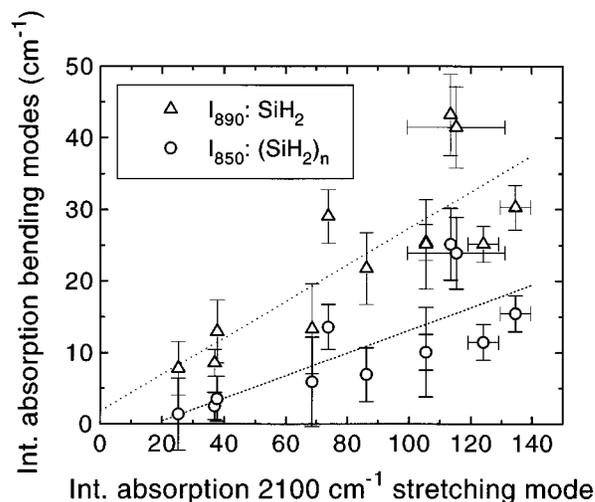


FIG. 4. Integrated absorption of SiH₂ bending and stretching modes.

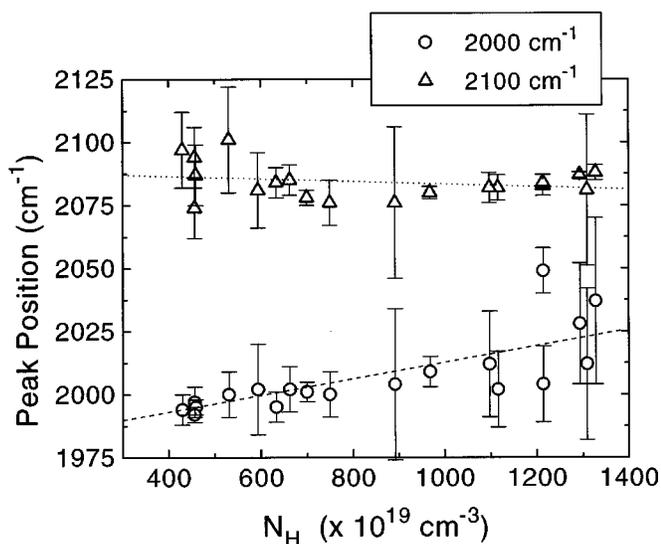


FIG. 5. Positions of the stretching mode peaks as a function of hydrogen content in the layer. Dotted and dashed lines are least squares fits through the data.

tent as determined from the sum of the two stretching modes at 2000 and 2100 cm^{-1} .

It has been suggested that clustered hydrogen and SiH on voids, even though it may be bonded in the SiH configuration, has its stretching mode near 2100 cm^{-1} .^{3,7} This would explain the observation that a large 2100 cm^{-1} peak corresponds to poor layer quality. Others have argued⁸ that a shift of 100 cm^{-1} of the stretching mode due to a different surrounding medium cannot be supported theoretically. Experimental results from Daey Ouwens *et al.*⁵ and Manfredotti *et al.*⁹ on PECVD deposited *a*-Si:H show that the integrated absorption at 2100 cm^{-1} is proportional to the integrated absorption of the SiH₂ bending mode at 890 cm^{-1} , for the PBD samples shown in Fig. 4. This means that if SiH on voids is assumed to have its stretching mode at 2100 cm^{-1} , it is necessary to assume that the amount of SiH on voids is proportional to the SiH₂ concentration in the layer. Further evidence to support the assumption that the shift in the vibrational frequency of SiH due to clustering is considerably less than 100 cm^{-1} is found if the position of the two stretch-

ing modes is considered. In Fig. 5 the position of the two peaks is shown as a function of the total hydrogen concentration. The position of the 2000 cm^{-1} peak changes with increased hydrogen concentration whereas the shift of the 2100 cm^{-1} peak is hardly distinguishable. This means that increasing the amount of clustering in the layer has an effect on the 2000 cm^{-1} peak, which suggests that clustered SiH should be associated with the 2000 cm^{-1} peak rather than the 2100 cm^{-1} peak. If the lines from Fig. 5 are extrapolated they intersect at a hydrogen density of approximately $3000 \times 10^{19} \text{ cm}^{-3}$, i.e., over 60 at. %, indicating that such a shift of 100 cm^{-1} is impossible to achieve.

To conclude, the measured dependencies of refractive index and band gap on hydrogen concentration for plasma beam deposited layers are similar to those reported for PECVD layers. Furthermore, the observed shift in the position of the SiH stretching mode frequency supports the conclusion from theoretical calculations⁸ that the shift caused by clustering of SiH is much less than 100 cm^{-1} , so that the 2100 cm^{-1} peak contains no SiH stretching contributions.

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