



## Polarized Raman spectroscopy analysis of SiH<sub>x</sub> bonds in nanocrystalline silicon thin films

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### ABSTRACT

For nanocrystalline silicon films deposited at high rates, the presence of a silicon–hydrogen (Si–H) bond stretching mode doublet in the high wavenumber region of the Raman spectrum can be used for optimizing the stabilized efficiency of solar cells based on this material. These peaks appear often for remote-plasma high deposition rate techniques targeting intrinsic layer deposition for photovoltaics, and so their structural origin may reveal the fundamental limitations of such techniques. We present the use of Polarized Raman Spectroscopy in oblique back-scattering configuration to reveal details of the specific bonding configuration of certain silicon–hydrogen bonds in hydrogenated nanocrystalline silicon (nc-Si:H). Twinned, narrow peaks located at 2083 and 2100 cm<sup>-1</sup> in the infrared absorption spectroscopy and Raman scattering spectrum of nc-Si:H thin films due to Si–H<sub>x</sub> stretching modes are strongly associated with films likely to oxidize and degrade rapidly, but the precise origin of these characteristic peaks is a subject of debate. Through the use of PRS, as well as numerous other complementary techniques (standard Raman scattering spectroscopy, Fourier transform infrared spectroscopy, Secondary ion mass spectrometry and X-ray diffraction), a logical conclusion can be reached, strongly suggesting that the origin of these peaks is due to the stretching modes of SiH<sub>2</sub> bonds at {110} interfaces between crystallites, passivated by hydrogen rather than by amorphous silicon. The use of the oblique back scattering Raman configuration, combined with group symmetry considerations, allows one to compare the symmetry of the vibrational modes detected with those of possible SiH<sub>x</sub> (X = 1, 2 or 3) configurations, thus eliminating certain structures as the sources of these characteristic absorption and scattering signatures.

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### 1. Introduction

Hydrogenated nanocrystalline silicon (nc-Si:H) has become a subject of active research owing to its lower gap and stability (relative to hydrogenated amorphous silicon) which makes it suitable for tandem solar cells in the so-called micromorph concept [1]. However, under specific process conditions but for multiple deposition technologies, the material can exhibit a porous structure has been correlated with the presence and evolution of a narrow doublet in the infrared absorption spectrum [2–4]. We have recently shown that this doublet – attributed to Si–H<sub>x</sub> stretching modes – can also be detected using Raman spectrometry [5], thus allowing one to perform the measurements on substrates suitable for solar cells. However, while a phenomenological link between the presence of this SiH<sub>x</sub> stretching mode doublet and an oxidation-related degradation in solar cell efficiency has been established [6,7], the detailed assignment of these peaks is still a matter of controversy [8–12]. Understanding the origin of the peak may be helpful in determining why certain deposition processes lead to their presence, and thus tend to produce films which oxidize rapidly whereas other similar ones do not.

As high deposition rate techniques using a remote plasma seem to be particularly prone to the occurrence of such peaks, this is a very relevant question for the future of such plasma sources.

We apply Polarized Raman Spectroscopy (PRS) as an additional tool for determining the origin of these peaks, an application for which it is particularly well suited as detailed information on the structural symmetries can be retrieved by studying the signal dependence on the polarization of the involved photons, as formally defined by the Raman scattering tensor [13]. The polarized nature of the Raman scattering phenomenon means that group theory, structural symmetry, Raman activity, and scattering geometry will determine the measured Raman spectrum. Due to this symmetry selectivity, PRS has recently been shown as an efficient and widely used optical tool for stress measurements on a wide range of semiconductor structures, in particular silicon-based ones [14–17]. PRS studies have also been performed to determine the orientation [18,19], as well as the structure and peak assignment [20] of molecular thin films.

### 2. Experiment

As in our previous studies, [5,8] the thin film investigated at in this work was deposited using a Matrix Distributed Electron Cyclotron

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Resonance Plasma Enhanced Chemical Vapor Deposition system [21], with a total injected microwave power of 1.5 kW into the seven antennas. A process pressure of 0.7 Pa was used, and gas-flows as follows: SiH<sub>4</sub>, Ar and H<sub>2</sub> of 8 sccm, 5 sccm, and 75 sccm, respectively. These process conditions lead to a deposition rate of  $\sim 5$  Å/s. The substrate temperature during deposition was 230 °C, as measured by pyrometry. The film was deposited on Corning Glass (EAGLE XG Slim glass, 1 × 1 in.) and was approximately 1 μm thick.

The PRS experimental setup shown in Fig. 1 is a high-resolution (0.1 cm<sup>-1</sup>) Raman spectrometer (Labram HR800 from HORIBA Jobin Yvon) operating in backscattering configuration with an excitation wavelength of 633 nm. In order to perform oblique incidence (off-axis) experiments, a long-working-distance objective (50×, NA = 0.45) is oriented at 65° with respect to the sample normal and produces an elliptical laser spot with approximate axis lengths of 2.5 μm × 1 μm. For the PRS experiments, a half-wave plate and an analyser inserted in motorized rotating mounts are used control the polarization states of the incident and scattered radiation, respectively, which can be continuously varied between 0° (*s* polarization; electric field perpendicular to the scattering plane) and 90° (*p* polarization; electric field parallel to the scattering plane) with 0.1° uncertainty. Note that, in the oblique incidence scattering geometry, the scattering plane is defined by the direction of the incident/scattered radiation and the sample normal; see Fig. 1.

### 3. Results

In the PRS study, we focus on the spectral range containing the Si–H<sub>x</sub> stretching vibrations (1900–2200 cm<sup>-1</sup>), and specifically on the doublet at 2083 and 2100 cm<sup>-1</sup>. This pair of sharp high wavenumber (HWN) peaks has been experimentally linked to the occurrence of rapid film oxidation and device degradation, but its origin and assignment remain controversial.

Fig. 2 presents the polarized oblique backscattering Raman spectrum collected in 180 s of the μc-Si:H thin film in the spectral range of interest. The spectrum was recorded for an incident (exciting) polarization state with a 90° azimuth (*p* polarization). Qualitatively similar Raman spectra, showing two broad features at 2000 cm<sup>-1</sup> and 2100 cm<sup>-1</sup>, were observed at other incident polarization states, too. For the analysis, the composite Raman spectrum was decomposed into a sum of five Gaussian peaks labeled *L<sub>i</sub>* (*i* = 1 to 5). In addition to the twinned peaks located at 2083 and 2100 cm<sup>-1</sup> and labeled L4 and L5 in the figure and three broad peaks can be observed, labeled L1, L2 and L3, although these are not the focus of this study.

In the PRS experiment, the azimuth of the incident polarization state was varied from 0° to 180° (through steps of 20°) by rotating the

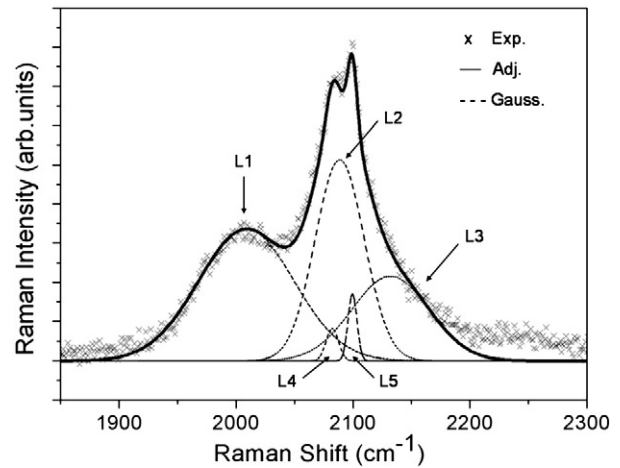


Fig. 2. Experimental Raman spectra of a μc-Si:H sample measured in oblique incidence backscattering configuration, for 90° incident polarization (“Exp”, crosses), numerical fit using five Gaussian peaks (*L<sub>i</sub>*, *i* = 1,...,5) after adjustment (“Gauss”, dashed lines), and the sum of the five peaks (“Adj”, solid line).

half-wave plate. At the same time, the analyzer, setting the polarization state of the scattered radiation, was kept fixed at 0° (*s* polarization).

Fig. 3 shows respectively the integrated intensity of the (a) L5 and (b) L4 as a function of the incident polarization azimuth. Both series of peak intensities exhibit the squared-sine-like behavior in accordance with the Raman selection rule (see below); however, the L4 intensity

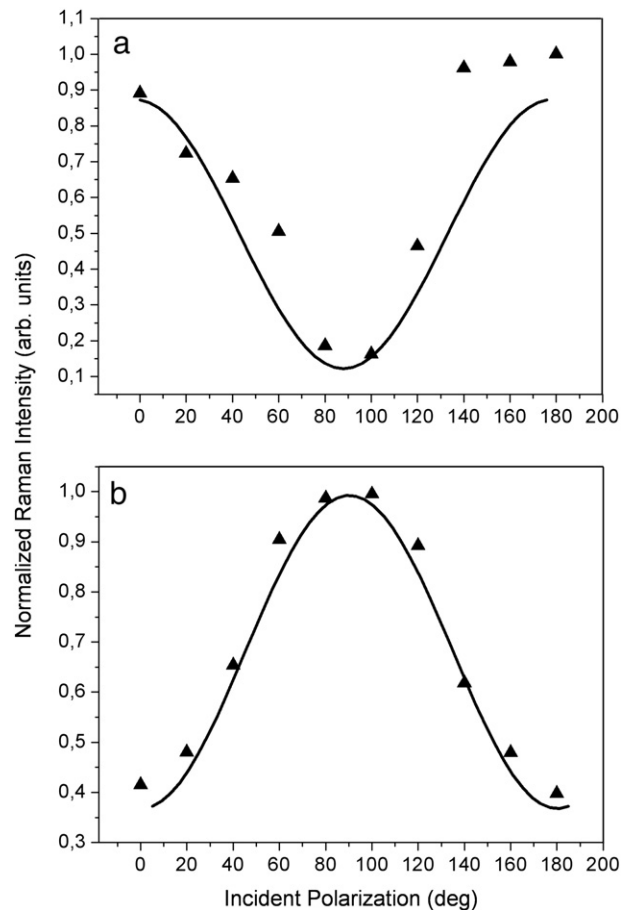


Fig. 3. Normalized Raman intensities of the Gaussian peaks L5 (a) and L4 (b) fitting the twin peaks at 2100 and 2083 cm<sup>-1</sup> (triangles), and the calculated intensities for a SiH<sub>2</sub> structure with a A<sub>1</sub> (a) and an B<sub>1</sub> (b) symmetry vibration modes (solid lines), as functions of the incident polarization.

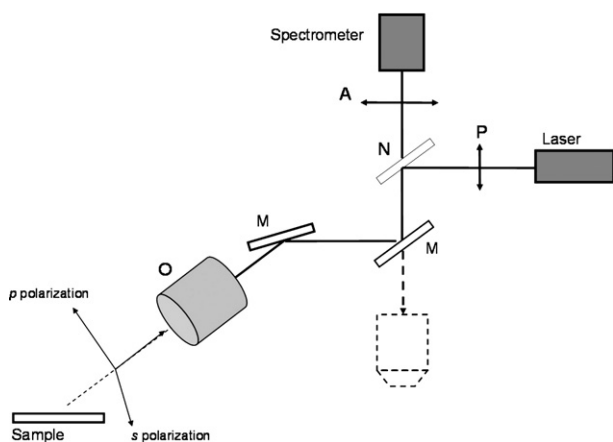


Fig. 1. Principle schematics of the experimental Raman scattering setup in oblique backscattering configuration: laser source (L), notch filter (N), polarizer (half-wave plate) (P), analyser (A), objective (O) and mirrors (M).

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