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Microstructure of hydrogenated silicon carbide thin films prepared by chemical vapour deposition techniques

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A B S T R A C T

We present the results of investigations on a variety of stoichiometric μc-SiC:H films deposited by Hot-Wire- and Plasma-Enhanced Chemical Vapour Deposition using monomethylsilane diluted in hydrogen as precursor gas. Infrared spectroscopy, grazing incidence X-ray diffraction, and Transmission Electron Microscopy were applied and compared to separate the contributions from the different structure phases of the material. It is shown that an evaluation of the crystalline volume fraction from the infrared absorption lineshape of the Si–C stretching mode is not possible, although stated in the literature. A correlation of this lineshape with the material strain is proposed. Moreover, a variation in strain, grain size, and structural defects is found depending on the deposition conditions, but a mixture of an amorphous and a crystalline phase could not unambiguously be identified.

1. Introduction

Recently, microcrystalline silicon carbide (μc-SiC:H) prepared by hot-wire chemical vapour deposition (HWCVD) has demonstrated its potential as a window layer in thin-film solar cells [1–4]. It is highly transparent for wavelengths in the visible light spectrum and still shows a reasonable conductivity [5,6]. However, if prepared from e.g. a mixture of Monomethylsilane (MMS) and hydrogen, large variations in the electronic properties are observed when deposition conditions are altered [5–10]. It is feasible to link these changes – similarly as in microcrystalline silicon – to a change of the microstructure of the material e.g. the crystalline volume fraction, which can be investigated directly with diffraction methods [9–12].

At present plasma-enhanced chemical vapour deposition (PECVD) is exclusively used for large area deposition of thin-film silicon solar cells. The preparation of device grade μc-SiC:H by PECVD would therefore be favourable. There are a few reports on silicon carbide deposited by PECVD [13,14], but there is no detailed investigation addressing its microstructure directly with diffraction methods. One aspect of the microstructure is the crystalline volume fraction. Its quantitative evaluation is rarely addressed for material deposited by either technique. A common procedure for estimating this value is the analysis of the infrared active Si–C stretching mode around 800 cm^{-1}, where the ratio of Lorentzian to Gaussian parts of the line profile f_{L-G} serves as a semi-quantitative value. In the literature, a Gaussian shape of this stretching mode is assigned to amorphous components of the material and a Lorentzian shape is attributed to a crystalline phase [15,16]. Consequently, a sum of those two peak profiles is fitted to the measured data while the relative contribution of the Lorentzian peak to the whole stretching mode yields the value for f_{L-G}. Although there are some comparisons between this parameter and the results of Raman scattering [17], sufficient links between f_{L-G} and the real microstructure of this material have not been presented so far. Even more, Raman spectra are difficult to interpret, when different structural phases are present, the material is strained, and the crystallite size is in the range of a few nanometres. In particular for silicon carbide thin films, the contribution of amorphous, cubic, and hexagonal phases is difficult to attribute unambiguously in the spectra [6].

Here, we report on the investigation of μc-SiC:H and amorphous silicon carbide (a-SiC:H) prepared by HWCVD and PECVD. The microstructure is addressed by evaluating f_{L-G} and the results of grazing incidence x-ray diffraction (GI-XRD). These results are supported by transmission electron microscopy (TEM) for selected samples. GI-XRD and TEM have got the striking advantage that the scattering cross section mainly depends on the atomic form factor, that is independent of the structural phase. Scattering intensities of different phases are thus directly proportional to their volume and can quantitatively be compared with each other.

2. Experimental

Microcrystalline silicon carbide thin films were prepared with PECVD and HWCVD. For both procedures monomethylsilane (MMS) diluted in hydrogen was used as a precursor gas. Doped samples were deposited with HWCVD using trimethylaluminum (TMAl) as

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dopant source and varying the flow ratios between TMAl and MMS (r_{doping}). More details on the deposition parameters can be found in Ref. [9]. The second series presented here was prepared using RF-PECVD with varying heater temperature T_s between 200 °C and 500 °C, while other parameters were kept constant. The plasma was excited with a frequency of 13.56 MHz and a power of 105 W. The concentration of MMS in hydrogen was 0.12% and the deposition pressure was about 400 Pa.

As substrates, chromium covered glass was utilised for GI-XRD measurements, and a silicon wafer for TEM and infrared spectroscopy (IR). A significant influence of the substrate on the structural growth of our material could not be found as shown by Heidt et al. [18].

$f_{\mathrm{L-G}}$ was obtained from Pseudo–Voigt profiles that were fitted to the infrared absorption modes. These profiles are a linear combination of a Lorentzian and a Gaussian function that have the same values for the full width at half maximum and are normalised to the same area. Due to the variation in the fitting results, we estimate the error of $f_{\mathrm{L-G}}$ to be around 15 percentage points.

GI-XRD was measured with a Bruker D8 Advance diffractometer in the parallel beam geometry. Cu–K_α radiation under incident angles well below 1° was applied to suppress scattering intensities from the substrate. For analysis of structural properties, thin TEM lamellae were covered with Platinum and prepared by the Focused Ion Beam (FIB) method. Using a Tecnai F20 TEM operated at 200 kV, diffraction patterns as well as microscopic bright field images were taken for selected samples to support the obtained results.

3. Results

The infrared absorption in the region between 500 cm^{-1} and 1100 cm^{-1} of selected samples prepared by HWCVD and PECVD is shown in Fig. 1a and b, respectively. Obviously, for a similar level of $f_{\mathrm{L-G}}$ the width of the Si–C stretching modes is considerably smaller for the samples prepared by HWCVD than for those prepared by PECVD. Moreover, a peak shift towards lower wavenumbers and a peak broadening with increasing r_{doping} and decreasing T_s is observed. As Table 1 indicates, $f_{\mathrm{L-G}}$ decreases with increasing r_{doping} except for the highest doping level, and it increases with increasing T_s.

Fig. 2a and b shows the results of GI-XRD measurements for the two series. In Fig. 2b, the background was subtracted and the diffractograms are normalised to their peak intensities for better illustration, which was not necessary for the series presented in Fig. 2a. For comparison, an amorphous reference sample was measured and included in Fig. 2a. The samples prepared by HWCVD showed reflections around 35°, 60°, and 70°, corresponding to the (111), (220), and (311)-planes of the 3C cubic lattice, respectively. Another reflection around 33.6° could be attributed to a hexagonal phase or planar defects [19]. Moreover, no signal similar to that of the amorphous reference sample could be detected. The dashed lines and the inset of Fig. 2a illustrate a shift in position for the observed reflections towards lower diffraction angles with increasing r_{doping} confirming the results of Miyajima et al. [7].

Table 1
Variation of the deposition parameters r_{doping} and T_s and corresponding $f_{\mathrm{L-G}}$ values. The error of $f_{\mathrm{L-G}}$ is estimated to be 15%.

r_{doping}	0%	1.6%	3.1%	6.2%	12.4%	15.5%
$f_{\mathrm{L-G}}$	93%	89%	77%	72%	16%	22%

T_s	200 °C	300 °C	350 °C	450 °C	500 °C
$f_{\mathrm{L-G}}$	0%	0%	7%	60%	64%

For the samples prepared by PECVD, the peaks are much broader. The {111}-reflections show a shift towards higher diffraction angles with increasing T_s. However, the reflections of higher order are too broad to draw clear conclusions. In addition, the sample prepared with the lowest T_s does not exhibit the three peaks related to the cubic structure, but two broad bands suggesting the absence of long range order.

The data were fitted using Pseudo–Voigt profiles in order to obtain information on the type of peak broadening. While the broadening caused by the crystallite size tends to result in a Lorentzian lineshape, a higher degree of microstrain will rather show a Gaussian type of broadening [20–22]. The broadening caused by the instrument is neglected because the narrowest peak shows a purely Lorentzian lineshape with a width of 0.36° (FWHM), while the instrumental broadening in that angular region was Gaussian-like and around 0.1° as determined by a polycrystalline Al_2O_3 reference sample.

Fig. 3 shows the dependence of the ratio η of Lorentzian to Gaussian contributions to the main XRD reflection around 35° on the variation of the deposition parameters. For the samples deposited by HWCVD, the peak broadening is almost purely Lorentzian type. For the PECVD series, the lineshape is completely Gaussian at low T_s and becomes nearly pure Lorentzian only at the highest T_s. The error of η is estimated to be around 0.1.

Fig. 5a shows a bright field TEM image of a film prepared by HWCVD with $f_{\mathrm{L-G}} = 72\%$. The contrast within the bright field images varies according to Bragg conditions, which differ as the crystallographic orientation changes with respect to the electron beam. Columnar crystal growth starts directly at the substrate. Most of the crystals are oriented perpendicular to the substrate and become larger in width with increasing film thickness. Additionally, a high density of various defects and voids was found. The diffraction pattern revealed a highly crystalline structure where the cubic phase prevails. The arc-like intensity distribution along the (111)-ring indicated a preferential orientation of the (111)-planes parallel to the growth direction.

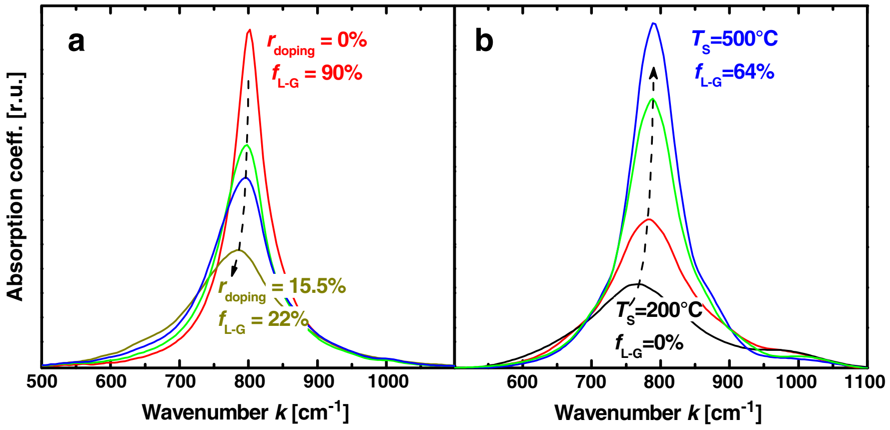

Fig. 1. Si–C stretching mode as measured by Infrared Spectroscopy for the series prepared by HWCVD with varying r_{doping} (a) and for the series prepared by PECVD with varying T_s (b).