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# Crystallization and Phase Separation of $Si_{1-x}C_x$ Films

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## Introduction

Thin films of silicon carbide ($Si_{1-x}C_x$) attract much attention for applications in various branches of technology [1-6]. Using magnetron sputtering, films of high quality with reproducible properties can be deposited on different substrates. After deposition the films are amorphous. Annealing at elevated temperatures leads to crystallization. Nucleation and growth processes during crystallization affect the microstructure of the polycrystalline films. For a tailored production of films for applications in microelectronics, optoelectronics or as protective surface coatings, detailed information of the crystallization process and the underlying kinetics is important.

For an understanding of crystallization of silicon carbide it is important to know the chemical order of the amorphous system which depends on the composition and on the production method. According to the tetrahedron model for amorphous silicon-carbon alloys given in reference [7], three types of chemical order can be considered: (a) complete random order where no preferential chemical bonding between Si and C atoms exists, (b) complete chemical order with homogenous dispersion which means that in Si-rich alloys a C atom in the centre of a tetrahedron is surrounded by four Si atoms and a maximum of possible Si-C bonds is realized and (c) complete chemical order with phase separation which means that the Si-C bonds are clustered.

Here, we investigate magnetron sputtered $Si_{1-x}C_x$ films with x=1/3 deposited on silicon wafers. For silicon rich $Si_{1-x}C_x$ films, a silicon phase can be expected in addition to the silicon carbide phase in the case of complete chemical order with phase separation. The aim of our work is the investigation of chemical order prior to crystallization.

## Experimental & Preparation

Thin films with a composition of $Si_{1-x}C_x$ (x=1/3) were prepared by RF co sputtering using a 3" US GUN low profile planar magnetron source (AP&T, Nürtingen, Germany) mounted on a standard DN 150 CF double cross recipient equipped with pre-sputter shutter and sample positioner. Deposition rates of 2–5 nm/min were achieved, using an operation pressure of $1 \cdot 10^{-3}$ mbar, a sputtering power of 80 W and a substrate temperature of 200 °C. Carbon stripes (99.99 %, Goodfellow, Bad Nauheim, Germany) of 5 mm x 25 mm were radially fixed at equal distances on a silicon base target (99.999 %, Norwegian Talc, Bad Soden, Germany), see figure 1 on the right. Films of 1 mm thickness were deposited on single crystalline silicon (111) wafers (CIS, Germany).

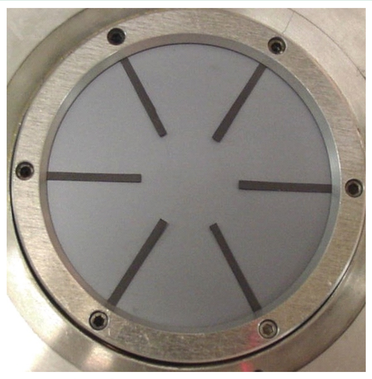


**Fig. 1** - Silicon base target

The samples were analysed with Grazing-Incidence X-ray diffractometry (GIXRD). Using GIXRD the X-ray strikes the sample under a small angle. The detector is moved while the sample is kept fix. Due to the small incident angle maximum information from the film is obtained while Bragg peaks from the substrate can be eliminated. We worked with a Siemens Kristalloflex/D5000 using Co $K_\alpha$ radiation (= 0.1789 nm, 40 kV, 40 mA). The grazing incidence angle was 5°. At this angle the substrate did not contribute to the diffractograms and a maximum count rate from the film was achieved.

X-ray Photoelectron Spectroscopy (XPS) is used for chemical analysis of the samples' surfaces. An ultrahigh vacuum apparatus with a base pressure of $5 \cdot 10^{-11}$ mbar is used to carry out preparation and spectroscopic measurements.
Electron spectroscopy is performed using a hemispherical analyzer (VSW HA100). A commercial non-monochromatic X-ray source (Specs RQ20/38C) is utilized for XPS. During XPS, X-ray photons hit the surface under an angle of 80° to the surface normal, illuminating a spot of several mm in diameter. For all measurements presented here, the Al $K_\alpha$ line with a photon energy of 1486.7 eV is used. Electrons are recorded by the hemispherical analyzer with an energy resolution of 1.1 eV under an angle of 10° to the surface normal. All XPS spectra are displayed as a function of binding energy with respect to the Fermi level. For quantitative XPS analysis, photoelectron peak areas are calculated after a Shirley background correction. Peak fitting with Gauss-type profiles was performed using OriginPro 7G including the PFM fitting module which uses Levenberg–Marquardt algorithms to achieve the best agreement possible between experimental data and fit.

## Results from GIXRD

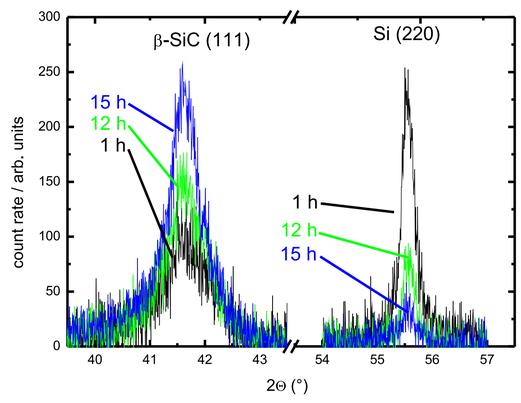



**Fig. 2** - GIXRD patterns of a 1 µm $Si_2C$ film deposited on a Si-wafer annealed at 1200 °C for different annealing times.

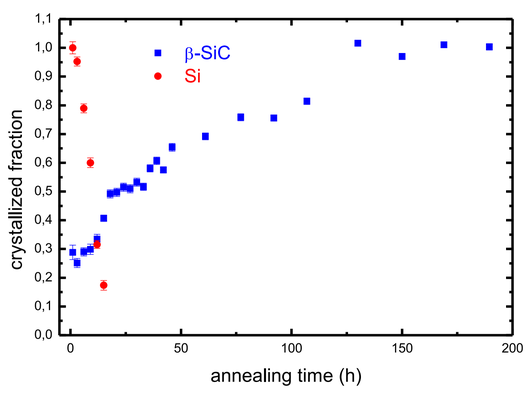


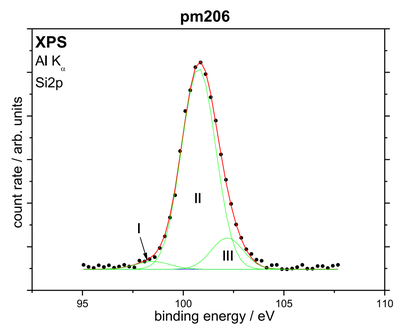

**Fig. 3** - Crystallized fractions of β-SiC and Si for a sample annealed at 1200 °C. The error bars at the data points correspond to the errors of the integrated areas determined by least-square fits with Lorentzian lines.

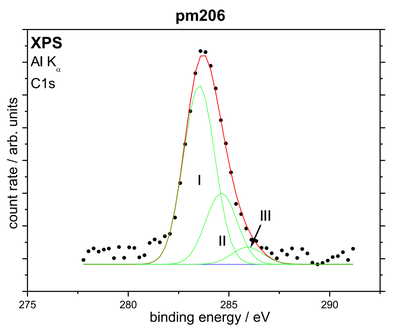
What is learned first, is the very slow crystallisation of a $Si_2C$ film. During annealing at 1200 °C in argon atmosphere, β-SiC is formed (Fig. 2). This takes place at large timescale of several hours (Fig. 3). The Si (220) signal in GIXRD declines towards a fraction of about 15 % just about after 15 hours. The question is raised if the Si atoms in the crystallizing film diffuse towards the substrate or to the upper surface layers.

At this point, XPS is used as a surface sensitive technique. Its information depth of about 10 nm and its ability to distinguish between different chemical bondings of surface structures is useful to investigate the raised question.

## Results from XPS

This section shows a $Si_2C$ sample which was only sputtered clean to reduce oxygen contamination.



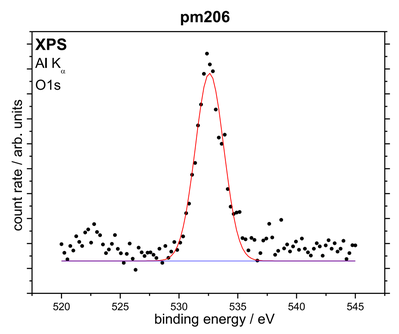




**Stoichiometry:**

Si 57.7 at.%
C 35.3 at.%
O 7.0 at.%

Si : C ratio*: 1.63

(*integral peak areas were used for the calculation)



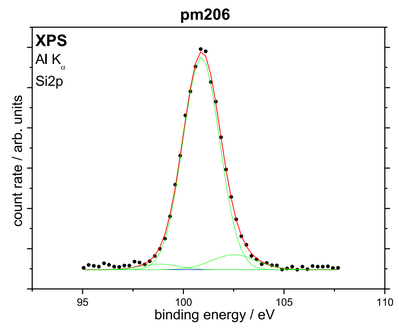

In detail, Si 2p and C 1s show three contributions (from lower to higher binding energy):

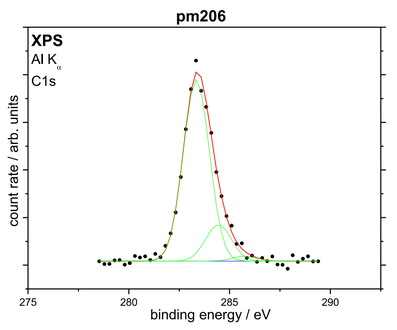
- **Si 2p:** Si - Si bonds, Si - C bonds, Si - O bonds
- **C 1s [8,9]:** C - Si bonds, C - C bonds ($sp_2$, $sp_3$ hybridisation)

Si 2p II : C 1s I ratio for unheated sample: 1.86

- O 1s shows one peak (532.6 eV) due to contamination

Sample heated up to 700 °C in UHV and held at this temperature for 60 min.



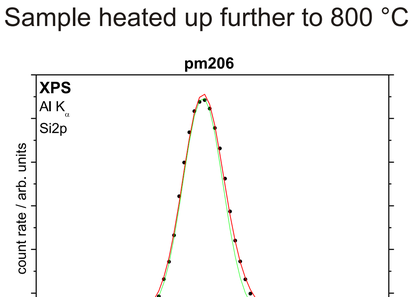

**Stoichiometry:**

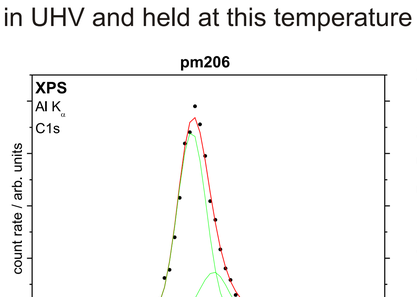
Si 61.8 at.%
C 35.8 at.%
O 2.4 at.%

Si : C ratio*: 1.72

Si 2p II: C 1s I ratio: 1.98

Sample heated up further to 800 °C in UHV and held at this temperature for 60 min.




**Stoichiometry:**

Si 63.3 at.%
C 33.9 at.%
O 2.8 at.%

Si : C ratio*: 1.87

Si 2p II: C 1s I ratio: 2.02

- Initially, heating of the sample leads to formation of stoichiometric $Si_2C$ at the surface and reduces the oxygen content
- XPS shows a trend towards Si enrichment at the surface with increasing temperature
- The assignment of the two contributions at higher binding energy in the C 1s is yet not clear [8,9]
- These first results will be further investigated via XPS, Metastable Induced Electron Spectroscopy (MIES), Ultraviolet Photoelectron Spectroscopy (UPS) and Temperature Programmed Desorption (TPD) and carried out at higher temperatures for comparison with the results from GIXRD

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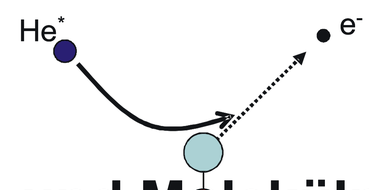


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