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Thermal stability of magnetron sputtered amorphous Si_2C

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ABSTRACT

The thermal stability of amorphous Si_2C films was studied by means of X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Grazing Incidence X-ray Diffractometry (GIXRD), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The films were deposited by magnetron sputtering onto silicon single crystals. The as-deposited films show a homogenous amorphous structure with a variety of bonding states reaching from homonuclear silicon-like Si—Si over mixed Si—Si—C to heteronuclear Si—C bonds. Annealing at 800 °C for 1 h leads to a depletion of Si—Si—C bonding states and to the formation of additional Si—C bonds. AFM and SEM images showed particles with a remarkable faceting on the surface of the annealed film. In accordance with GIXRD and AES measurements, these observations confirmed the crystallization of silicon during thermal annealing. Besides, no crystallized silicon carbide could be detected.

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1. Introduction

Non-stoichiometric $Si_{1-x}C_x$ films attract much attention for applications in various branches of technology, especially in the fields of electronics, optoelectronics and photovoltaics. Typical examples are window layers in solar cells [1], insulating layers in thin film transistors [2], thin film light emitting diodes [3,4], color displays [5], UV detectors [6], Li ion battery anodes [7], microelectro-mechanical systems (MEMS) [8] and many more. A current research field is the design of silicon quantum dots embedded in an amorphous matrix of silicon carbide [9,10]. For these applications a fundamental understanding of the amorphous to crystalline transition is of large importance, especially for Si-rich films of composition $Si_{1-x}C_x$ ($x < 0.5$).

Using magnetron sputtering, films of high quality with reproducible properties can be deposited on various 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. In a recent study [11], the crystallization kinetics of amorphous Si_2C films were investigated by Grazing Incidence X-ray Diffractometry (GIXRD) at temperatures between 1200 °C and 1350 °C. Here, a transient formation of crystalline Si was found to be superimposed by stoichiometric SiC crystallization.

For the understanding of these processes, the chemical order of the amorphous system, which depends on the composition and on the production method [12], is of importance as well as the early stages of crystallite formation. According to the tetrahedron model for amorphous silicon–carbon alloys given in [13], 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 that a maximum of possible Si—C bonds is realised; and (c) complete chemical order with phase separation, which means that the Si—C bonds are clustered [13]. Molecular dynamics simulations suggest [14] that 40–45% homonuclear bonds are present in stoichiometric amorphous silicon carbide. However, the same simulations also revealed a high degree of short- and medium-range order excluding a complete random order.

In the present work we studied the structure and the thermal stability of amorphous Si_2C and the early stages of surface crystallization at 800 °C by means of X-ray Photoelectron Spectroscopy

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(XPS), Auger Electron Spectroscopy (AES), Grazing Incidence X-ray Diffractometry, Atomic Force Microscopy and Scanning Electron Microscopy (SEM).

2. Experimental details

Thin amorphous films of silicon carbide (Si_2C) were prepared by a r. f. cosputtering technique using a 300 US GUN low profile planar magnetron source (AP&T, Nürtingen, Germany) mounted on a standard DN 150 CF double cross recipient equipped with presputter shutter and sample positioner allowing various distances (100–200 mm) between magnetron and substrate. Deposition was done at a rate of 5 nm/min, using an operating pressure of 1×10^{-3} hPa, a sputtering power of 80 W, and a substrate temperature of 200 °C. Carbon stripes (99.99%, Goodfellow, Bad Nauheim, Germany) of 5 mm × 25 mm were radially fixed at equal distances on a silicon base target (99.999%, Norwegian Talc, Bad Soden, Germany). The films were deposited on single crystalline silicon (1 1 1) wafers (CIS, Germany). Measurements with Rutherford Backscattering Spectrometry (RBS) revealed a Si:C ratio of 2:1 [15].

X-Ray Photoelectron Spectroscopy was carried out in an ultra high vacuum (UHV) apparatus with a base pressure of 5×10^{-11} hPa [16]. All XPS measurements were performed at room temperature. Annealing of the films was performed in situ inside the ultra high vacuum using a sample heater based on electron impact heating of the backside of the sample. The UHV apparatus is equipped with a preparation chamber, containing an Ar^+ sputter gun for additional cleaning procedures.

XPS is performed using a hemispherical analyzer (VSW HA100) and a commercial non-monochromatic X-ray source (Specs RQ20/38 C). During XPS, X-ray photons irradiate the surface under an angle of 80° to the surface normal, illuminating a spot with a diameter of several mm. For all measurements presented here the Al Kα line (photon energy 1486.6 eV) is used. Electrons are recorded by the hemispherical analyzer with an energy resolution of 1.1 eV emitted under an angle of 10° to the surface normal.

The transmission function of the analyzer has been previously determined by experiment. All XPS measurements were corrected for this transmission function. 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 via mathematical fitting with Gauss-type profiles using OriginPro 7G including the PFM fitting module, which applies Levenberg–Marquardt algorithms to achieve the best agreement possible between experimental data and fit. Photoelectric cross sections as calculated by Scofield [17] and inelastic mean free paths from the NIST database [18] as well as the energy dependent transmission function of our hemispherical analyzer are taken into account when calculating stoichiometry.

For the characterization of the crystallographic structure of the films, the samples were analyzed by Grazing Incidence X-ray Diffratometry. Using GIXRD the X-rays strike the sample under a small angle. The detector is moved while the sample is kept fixed. 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 Kα radiation ($\lambda = 0.1789$ nm, 40 kV, 40 mA). A rocking curve was recorded before each GIXRD measurement to eliminate a possible tilt angle of the sample. 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.

The topography of the as-deposited Si_2C and the annealed Si_2C-surfaces is determined by Atomic Force Microscopy using a Veeco Dimension 3100 SPM. All measurements are performed in tapping mode with Al-coated silicon cantilevers (NSC15, Micromasch). The typical resonant frequencies of this series are about 325 kHz, typical spring constants are in the range of 40 N/m. The radius of the tip curvature is less than 10 nm. All images consist of 512 lines each containing 512 pixels. They are recorded with a line-scan frequency of 0.7 Hz. SPIP (Image Metrology A/S) is used for the depiction of the AFM images and the calculation of the average surface roughness (RMS) according to ISO 4287/1.

AES and SEM were carried out in a Scanning Auger Electron Microscope (Omicron NanoSAM) with a base pressure below 10^{-10} hPa. The spatial resolution of 5 nm for AES and about 3 nm in SEM mode makes is suitable for the characterization of small structures. All SEM images were taken with a primary electron energy of 5 keV.

AES is also performed at an electron energy of 5 keV and an incident electron beam of 1.0 nA using a hemispherical analyzer.

3. Results and discussion

3.1. As-deposited Si_2C

The XPS survey spectrum of the as-deposited Si_2C film is presented in Fig. 1a. The sample was previously sputtered with Ar^+ to remove surface contaminations like oxygen and carbon. The survey spectrum shows distinct elemental peaks of silicon, carbon and oxygen which can be typically expected. Moreover, additional peaks can be found representing argon and molybdenum, originating from argon incorporations due to the sputter deposition process and from the sample holder, respectively. The global stoichiometry contains 58% silicon, 36% carbon and 6% oxygen, resulting in a global Si/C ratio of 1.6. This value is in striking difference to the one obtained by Rutherford-Backscattering Spectroscopy measurements mentioned above. The XPS detail spectra of the Si_2p and C1 s regions are shown in Fig. 1(b) and (c). Due to the plain background observed for the C1 s and O1 s structures, a linear background subtraction was applied, whereas a Shirley correction is used for Si_2p before the fitting procedure. Peak widths (full width at half maximum, FWHM) and binding energies from preliminary experiments on Si(1 0 0) and SiC(0 0 0 1) single crystals were used as reference data for the fits, as well as additional literature [19,20]. The Si_2p spectrum in Fig. 1b shows a symmetric line shape, exhibiting a small shoulder towards higher binding energy. Considering the tetrahedron model of amorphous silicon carbide introduced by K. Mui and F. W. Smith [13], the peak is fitted with several components assigned to homonuclear Si—Si, heteronuclear Si—C and a mixture of Si—Si—C bonds. Besides, there is a fourth peak representing bridging oxygen or silicon oxycarbide [21]. The low amount of Si—C bonds is striking. The major contributions accounts for Si—Si—C, indicating that there is only a small preference for Si—C bonding in the amorphous phase. The C1 s spectrum in Fig. 1c contains both heteronuclear C—Si and homonuclear C—C bonds, as well as C—O in a limited extent. The C—C bonded carbon species has an chemical shift of 1.9 eV relative to the C—Si peak and could be identified as diamond-like carbon. The C—C and C—O bonded carbon species might belong to the deposited Si_2C film, as well as originate from carbon contaminations located on the sample holder. Those contaminations may explain the underestimated Si/C ratio of 1.6, compared to the value of 2.0, obtained by RBS.

No other carbon species, like mixtures of Si—C—C for example, could be found, which is in good agreement with the predictions of the tetrahedron model for silicon-rich amorphous Si_2C [13].

All XPS data like binding energies, peak widths and the relative intensities of the corresponding species with regard to the elemental peaks, are summarized in Table 1.

Fig. 2 shows the GIXRD diffractogramms of the as-deposited Si_2C sample (bottom). Characteristic Bragg peaks, indicating the

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