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High temperature annealing effects on the chemical and mechanical properties of inductively-coupled plasma-enhanced chemical vapor deposited a-SiC:H thin films

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ABSTRACT

This paper reports the impact of thermal annealing up to temperatures of 1200 °C on the chemical and mechanical properties of hydrogenated amorphous silicon carbide (a-SiC:H) thin films. These layers were deposited using an inductively-coupled plasma-enhanced chemical vapor deposition process with methane, silane and argon as precursor gases. The results of mass effusion measurements up to 1000 °C are presented and the temperature-dependent effusion characteristics are compared to changes in the Fourier-transform infrared spectra. Furthermore, a simple method is presented that enables us to detect the onset of nanocrystallization in the a-SiC:H films caused by the high temperature annealing. The changes in chemical and crystallographic properties are discussed and related to the mechanical thin film properties, such as a substantial increase in Young's modulus from 176 up to 267 GPa, in hardness from 24 up to 34.5 GPa, as well as in residual film stress from −683 up to +3800 MPa. Additionally, the decrease in layer thickness to about 70% of the initial value and the increase in refractive index from 2.33 to 2.78 are explained.

1. Introduction

In microelectromechanical systems (MEMS) the need of highly robust and rigid materials is growing continuously to enable the operation of systems under high temperatures or in corrosive environments [1]. Silicon carbide (SiC) as a wide bandgap semiconductor features many outstanding mechanical and electrical properties. It provides a high temperature stability, features enhanced Young's modulus (E) and hardness (Γ) values and a high chemical inertness against corrosive environment and is therefore a promising material for high performance MEMS devices [2]. SiC is available as substrate material or can be deposited as a thin film either as passivation layer [3] or within surface micromachined devices [4]. Crystalline SiC (c-SiC) exists in various polytypes and modifications. It provides superior electrical and mechanical properties, but its fabrication is relatively complex compared to standard silicon and therefore expensive. It is widely used for high power electronic devices, like SiC Schottky diodes where the use of SiC provides lower switching losses and higher operation temperatures [5,6]. Polycrystalline SiC is for example used for pressure sensors [7] or micro-heaters [8] and can be synthesized via chemical vapor deposition (CVD) on Si substrates. Nowadays, deposition of polycrystalline SiC requires temperatures of 1050 °C and above which reduces the available process steps and materials during MEMS fabrication [9]. To lower the temperature necessary for thin film synthesis, nanocrystalline hydrogenated SiC (nc-SiC:H) can be deposited by a radio-frequency magnetron sputtering process [10,11] while synthesis of hydrogenated amorphous SiC (a-SiC:H) is possible via plasma-enhanced CVD (PECVD) at 400 °C and below. Despite the hydrogen (H) incorporation and the amorphous state, many outstanding properties of SiC are still preserved to a certain degree. a-SiC:H is for example used as a matrix material for photovoltaic applications to form Si nanocrystals via a subsequently applied annealing step [12,13] or as a chemically inert and up to 650 °C thermally stable passivation layers to improve the device properties [14].

Due to the high hydrogen content, many key properties of a-SiC:H films can be modified to a great extent via post-deposition annealing. This leads to an extreme diversity and adjustability of the a-SiC:H layer characteristics for the application in high-performance MEMS devices. Annealing effects on optical properties and film stress of a-SiC:H thin films up to temperatures of 600 °C in air were presented in [15], describing a reduction of hydrogen content and a subsequent evolution of tensile film stress. Formation of Si and/or SiC nanocrystals due to thermal treatment in an a-SiC:H matrix and the dependency on the Si and C content of the layer is described in [16–18]. Although much effort is

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invested in the detailed characterization on a large variety of film properties, a direct correlation to the effusion of gaseous species like hydrogen or residues of the precursor gases is, to the best of the authors' knowledge, still missing.

It is the objective of this study to investigate the impact of thermal annealing up to 1200 °C under vacuum conditions on the chemical and mechanical properties of inductively-coupled plasma-enhanced CVD (ICP-CVD) a-SiC:H thin films. The corresponding changes in chemical composition and microstructure are explained and correlated to modifications of residual stress, Young's modulus and hardness. Furthermore, mass effusion measurements up to temperatures of 1000 °C are performed to reveal the influence of the effusing species on these key material parameters for MEMS devices.

2. Experimental details

An overview about the sample preparation and measurement cycle is provided in Fig. 1. As substrates, 350 μm thick, double side polished 4″ Si (100) wafers were used. The surface was cleaned with an EVG EV 300 megasonic wafer cleaner and the natural oxide layer was removed, using a 12% buffered HF etching solvent prior to deposition. The a-SiC:H thin films were synthesized using an OXFORD INSTRUMENTS Plasmalab ICP-CVD System 100 at a substrate holder temperature of 250 °C. Gas flow rates were 13.5 sccm methane (CH_4), 6.5 sccm silane (SiH_4) and 50 sccm argon (Ar). Deposition time was set to achieve a layer thickness of 300 nm and 600 nm at an inductively-coupled plasma power of 2000 W at a radio frequency (RF) of 13.56 MHz. The chamber pressure was 6 mTorr. Thermal loading was applied for 1 h each, using an UniTemp RTP-100-HV rapid thermal annealing furnace under vacuum conditions up to temperatures of 1200 °C. The thickness and the refractive index of the layer at $\lambda = 632.8$ nm were measured with a Filmetrics F20-UVX spectral reflectance meter after deposition and after each annealing step. Additionally, the film stress was determined using an E + H Metrology MX203-6-33 wafer bow measurement equipment. The Fourier transform infrared (FT-IR) spectra were recorded with a BRUKER TENSOR FT-IR spectrometer, measuring the IR absorbance at the center of the wafer. The measured FT-IR spectra were processed by subtracting the Si-substrate reference spectrum.

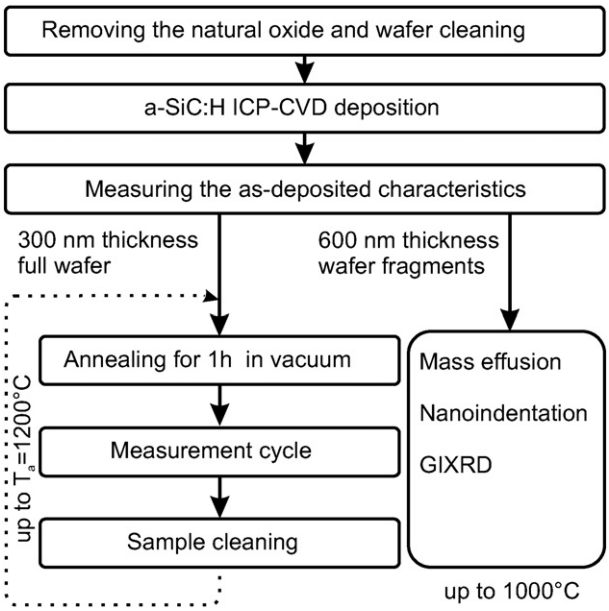

Fig. 1. Description of sample preparation and measurement cycle.

Additionally, a polynomial baseline fit of the spectra was obtained and the absorption coefficient $\alpha(\omega)$ calculated, following the Beer–Lambert law

$$\alpha(\omega) \cdot t = -\ln\left\{\frac{I(\omega)}{I_0(\omega)}\right\}, \quad (1)$$

where t is the thickness of the layer and $I(\omega)$ and $I_0(\omega)$ are the intensities of the incident and the transmitting radiation, respectively [19]. The deconvolution of certain vibration modes is achieved by using either Gaussian or pseudo-Voigt functions, which yields good fitting results. To determine E and Γ of the thin films, nanoindentation measurements were performed using a Fischer-Cripps Laboratories UMIS nanoindenter equipped with a Berkovich diamond tip. Load–displacement curves were recorded applying loading forces from 3 up to 45 mN and analyzed using the Oliver–Pharr-method [20]. For effusion measurements, a sample of 1.5×1.5 cm^2 size was loaded onto a heating plate and a temperature ramp of 5.33 °C min^{-1} was applied up to 1000 °C. At 1000 °C, the temperature was fixed for 1 h to allow the probe to fully degas. Effusion of gaseous species with different masses was detected with a HIDEN HALO RGA spectrometer. Additionally, a reference spectrum of a pure Si substrate sample, having the same dimensions as the a-SiC:H probe, was used to determine the background spectra. X-ray diffractograms (XRD) are obtained from a PANalytical Empyrean diffractometer, using the Cu Kα radiation line. Due to the low crystallinity and thickness of the samples, the gracing incident XRD (GIXRD) approach is applied. The angular resolution for all measurements was 0.02° and the diffracted radiation at each data point was accumulated for 4.2 s.

3. Results and discussion

3.1. Effect of annealing on the chemical and crystallographic properties

An overview of the annealing effect on the FT-IR spectra is shown in Fig. 2 for selected temperatures, revealing a substantial impact of temperature on the chemical composition and bonding properties in the thin film. The most dominant vibrational peaks are labeled in Fig. 2: a broad peak from 470 to 1100 cm^{-1} containing several Si–C stretching modes [21], a Si–H_x bending and rocking mode [22] and an additional peak for the C–H_2 wagging mode from the Si–C–H_2 complex. A peak around 2100 cm^{-1} represents the Si–H_x stretching vibrations and a peak at 2875 cm^{-1} the C–H_x stretching vibrations [23]. Annealing causes a reduction of hydrogen containing bonds and a massive increase in peak height of the strong Si–C stretching mode, which can be explained by effusion of

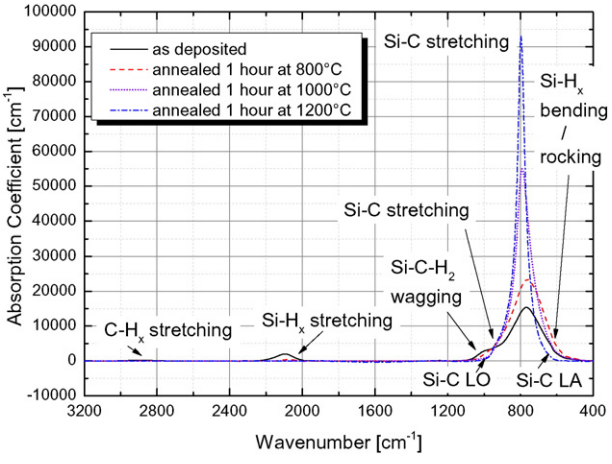

Fig. 2. Impact of annealing on the resulting FT-IR spectra, shown for selected temperatures. Most important vibrations are labeled.