



Highly retarded crystallization in hydrogenated amorphous germanium; emergence of a porous nanocrystalline structure

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ABSTRACT

The thermal crystallization of heavily hydrogenated, amorphous Ge (*a*-Ge:H) and ultra-pure amorphous Ge (*a*-Ge) thin films was investigated, on a comparative basis, by X-ray diffraction and high-resolution transmission electron microscopy (HRTEM) performed during *in situ* heating. It was found that the crystallization process in *a*-Ge:H is pronouncedly retarded, due to the initial presence of hydrogen-induced nanovoids. The crystallization of *a*-Ge:H initiates only after considerable reduction of the amount of nanovoids in the amorphous matrix by thermally induced coarsening of the nanovoids leading to nanopores in the *a*-Ge:H. Such retarded crystallization leads to the formation of nanocrystalline, porous Ge with nanocrystal sizes below 20 nm, in contrast with the fast formation of very large-grained (grain sizes of hundreds of nanometer) polycrystalline Ge upon thermal crystallization of pure *a*-Ge.

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1. Introduction

Ge and Ge-based materials have a wide range of applications in electronics and optoelectronics, e.g. as multi-junction solar cells, photodiodes, and infrared photodetectors [1–4]. Ge thin films grown from vapor phases at low temperatures are usually amorphous with unfavorable properties [5]. A transformation of the amorphous state to the crystalline state thus is imperative in view of the above-described technological applications [6,7]. Against this background, fundamental understanding of the crystallization mechanism of amorphous Ge (*a*-Ge), and particularly the impact of the initial amorphous structure on the crystallization, is therefore required.

Hydrogen is usually, often naturally, introduced into amorphous Ge thin films during their deposition [1,2,8,9]. Hydrogen incorporation can profoundly modify the microscopic/atomic structure of the film, e.g. by reducing the amount of dangling bonds, and therefore its properties (e.g. density, thermal conductivity, crystallization behavior) [2,10]. Hydrogen incorporation during amorphous film growth can further lead to the formation of free volume in the form of nanosized voids (nanovoids), where hydrogen atoms “occupy” dangling bonds at the internal surface [11]. Although the crystallization process of pure *a*-Ge has been extensively investigated in the past [12–15], only a few reports

deal with the crystallization mechanism of hydrogenated amorphous Ge (*a*-Ge:H) [16,17]. A comprehensive picture of the microstructural changes taking place during the crystallization of *a*-Ge:H is not available.

In this work, the thermally induced crystallization behaviors of pure *a*-Ge and hydrogenated amorphous Ge (*a*-Ge:H), both deposited at room temperature by ultrahigh-vacuum (UHV) thermal evaporation in a highly controlled manner, were investigated, on a comparative basis, by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) performed during *in situ* heating. The crystallization mechanisms could thus be exposed. It was found that the incorporation of hydrogen, leading to nanovoids, pronouncedly retards the crystallization of *a*-Ge:H. Crystallization sets in only after removal of a majority of the nanovoids from the amorphous matrix by thermally induced coarsening of the nanovoids leading to nanopores (with a characteristic size of about 10 nm) in *a*-Ge:H. Such retarded crystallization was shown to lead to the formation of nanocrystalline, porous Ge (with crystallite sizes <20 nm), even at annealing temperatures as high as 530 °C.

2. Experimental procedures

2.1. Thin film deposition and *in situ* characterization

The deposition of *a*-Ge and *a*-Ge:H thin films was carried out in a custom-built ultrahigh vacuum molecular beam epitaxy system (base pressure < 2×10^{-10} mbar). Si₃N₄ (50 nm)/SiO₂ (50 nm)/Si wafers (for *in situ* spectroscopic ellipsometry and *in situ* heating XRD

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experiments) and 20-nm thin SiO₂ membranes (purchased from Simpure Inc. and intended for *in situ* heating HRTEM experiments) were used as substrates. Before deposition, the substrates were thoroughly degassed in UHV at about 250 °C for 1 h. Pure *a*-Ge and *a*-Ge:H thin films were then deposited onto the substrates at room temperature with deposition rates of 1.7 nm/min and 1.8 nm/min, respectively. Ge was supplied by thermal evaporation of pure Ge (>99.999 wt.%) from a pyrolytic graphite (PGR) crucible using a high-temperature effusion cell (type HTC-40-2-250-WK-SH by Createc GmbH, Germany) at 1400 °C. For the deposition of the *a*-Ge:H thin films, a flux of atomic hydrogen, which was generated by passing H₂ gas through a high-temperature cracker cell (type HCL by Createc GmbH, Germany) operated at about 2000 °C, was directed towards the substrate surface concurrently with the Ge atomic flux. The chamber pressure increased to about 3.4×10^{-6} mbar due to the introduction of the hydrogen gas (at a flux rate of 0.002 standard cubic centimeters per minute through a differential pumping setup) during deposition of the *a*-Ge:H films.

After deposition, the as-deposited pure *a*-Ge and *a*-Ge:H specimens were subjected, without breaking the vacuum, to spectroscopic ellipsometric (SE) analysis employing a J.A. Woollam M2000 ellipsometer (wavelength range of 245–1000 nm). The as-measured SE data were modeled by using a three-layer optical model comprising the substrate, the *a*-Ge (or *a*-Ge:H) layer and a surface-roughness layer (*cf.* Ref. [18]). The real and imaginary parts of the dielectric function of the substrate were determined by SE measurement of a bare substrate; those of *a*-Ge and *a*-Ge:H were modeled with the Tauc-Lorentz dispersion model [19]. On this basis, the dielectric functions and the film thicknesses of the as-deposited *a*-Ge and *a*-Ge:H films were determined by fitting of the as-measured SE data. The fitting showed that the *a*-Ge and *a*-Ge:H films are 64 nm and 72 nm thick, respectively.

After SE measurements, the films were covered either by a 20-nm thick amorphous Si (deposited by thermal evaporation) or an 8-nm thick amorphous SiC (deposited by radio-frequency sputtering) layer, in order to prevent a possible oxidation of the layer by oxygen from the environment. The thus capped films were then used for *in situ* heating XRD and *in situ* heating HRTEM experiments.

The intrinsic stresses generated in the pure *a*-Ge and *a*-Ge:H films were measured *in situ* during growth by a multi-optical stress sensor (k-Space Associates), based on the laser-optical measurement of the curvature change of the substrate (which was loosely mounted in the specimen holder) [20], and by applying Stoney's equation [21].

2.2. *In situ* heating XRD experiments and subsequent TEM analysis

The *in situ* heating XRD experiments were performed in Bragg-Brentano geometry on a Bruker D8 Discover diffractometer equipped

with a Cu K α X-ray source ($\lambda = 1.54056$ Å) utilizing parallel beam geometry and a heating/cooling stage (Anton Paar DCS350) which was calibrated as described in Refs. [22–24]. An X-ray transparent dome made of polyetheretherketone was mounted on top of the heating plate, which allowed a vacuum (with a residual pressure of about 1 Pa) to be applied during the entire *in situ* heating XRD experiments. The temperature was increased from room temperature up to 509 °C in steps of 17 °C and at each temperature step θ - 2θ scans ($2\theta =$ diffraction angle) were recorded in the 2θ range of 26° to 28°. Each temperature step involved annealing for 35.5 min, and the XRD θ - 2θ scans were acquired during the last 20.5 min of this annealing. After the *in situ* heating XRD experiments (*i.e.* after the last anneal at 509 °C and naturally cooling to room temperature), the microstructures of the crystallized pure *a*-Ge and *a*-Ge:H specimens were investigated by cross-sectional TEM in a Philips CM 200 microscope operated at 200 keV. The used cross-sectional TEM specimens were prepared using the method as described in Ref. [25].

2.3. *In situ* heating HRTEM experiments

The *in situ* heating HRTEM measurements were performed in a JEOL ARM-1250 high-voltage electron microscope which is operated at 1250 keV with a point-to-point resolution of 0.12 nm and is equipped with a drift compensator (see *e.g.* Ref. [25]). The base pressure in the TEM specimen chamber is about 2×10^{-6} Pa. The *in situ* annealing was carried out using a Gatan 652-Ta double-tilt heating stage. During *in situ* annealing, the HRTEM images were recorded either on a real-time charge coupled device video camera (25 frames per second) or on photographic negatives. The *in situ* annealing HRTEM experiments were carried out for the pure *a*-Ge film at 467 °C and 500 °C, and for the *a*-Ge:H film at 500 °C and 530 °C. A heating rate of about 50 °C/min was used to heat the specimen up to the aimed temperatures. For each investigated specimen the *in situ* heating HRTEM characterization was carried out continuously until full crystallization had been achieved.

3. Results and discussion

3.1. Characterizations of as-prepared *a*-Ge and *a*-Ge:H films

The incorporation of hydrogen into the matrix of the *a*-Ge:H film during its deposition by thermal evaporation leads to a microstructure of the *a*-Ge:H film pronouncedly different from that of the pure *a*-Ge film.

The as-deposited *a*-Ge:H and *a*-Ge films possess distinctly different dielectric functions, as revealed by the *in vacuo* spectroscopic

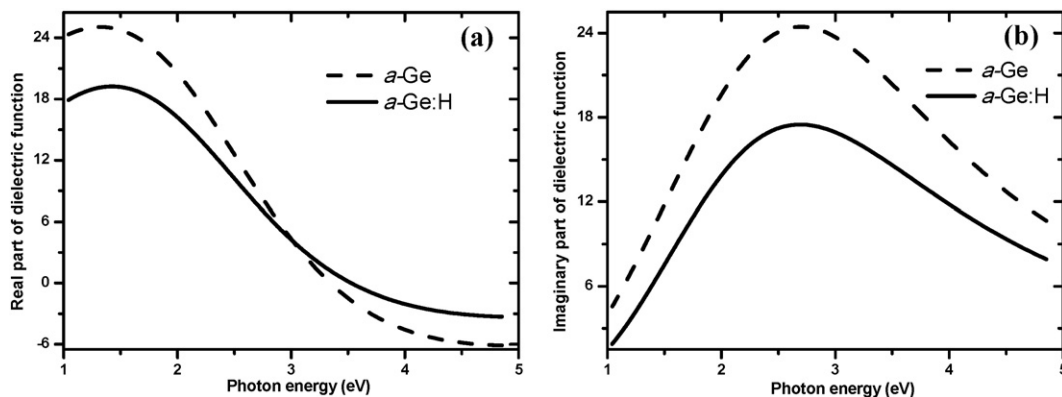


Fig. 1. (a) Real and (b) imaginary parts of the dielectric functions of the as-deposited pure *a*-Ge (dashed line) film and the *a*-Ge:H film (solid line) as determined by *in situ* spectroscopic ellipsometry and fitting with the Tauc-Lorentz dispersion model.

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