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Ellipsometric study of crystallization of amorphous Ge thin films embedded in SiO_2

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Abstract

We use spectroscopic ellipsometry to investigate crystallization of amorphous Ge thin films by thermal annealing of SiO_2/*a*-Ge/SiO_2 trilayer structures. We study the influence of both film thickness and annealing temperature on the effective dielectric functions of the Ge films, which are related to the film micro- and nanostructures. For annealing temperatures below 900 °C, all films remain continuous and consist of mixtures of amorphous and nanocrystallized Ge. The crystallite sizes can be estimated from the observed energy blueshift of the E_1 interband transition. Samples annealed at 900 °C display dielectric function spectra which differ from a bulk-like behavior. This suggests a variation in optical properties which is correlated to formation of discontinuous films of Ge nanocrystals.

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1. Introduction

Ge nanocrystals embedded in SiO_2 have attracted a strong interest in the scientific community due to their potential applications in optoelectronics as light emitters, and in high-speed, low-power logic and memory devices [1,2]. A promising way to synthesize Ge nanocrystals within a SiO_2 matrix film is by high-temperature annealing of SiO_2/*a*-Ge/SiO_2 trilayer structures [3]. The kinetics and thermodynamics involved in the nucleation and growth process play a key role in obtaining a suitable distribution of nanocrystals with specific size. As a part of a comprehensive study of melting and crystallization of *a*-Ge thin films [4] we have used spectroscopic ellipsometry for characterization of trilayer samples after different processes of thermal annealing. We studied the different obtained films depending on the initial *a*-Ge thickness, nominally varied between 10 and 50 nm, and the annealing temperature between 400 and 900 °C. Ellipsometry allowed us to draw conclusions about sample structures and the consequent changes in their electronic properties.

2. Experiments and data analysis

The samples consisted on a trilayer structure SiO_2(cap)/*a*-Ge/SiO_2(buffer) deposited by e-beam evaporation on an oxidized Si substrate. All studied samples were similar except for the thickness of the *a*-Ge film, which was set to nominal values of 10 and 50 nm. Films were deposited on a same 4″ Si wafer that was cut into pieces of ~1 cm^2 to follow different annealing treatments. Each sample was annealed once, in high vacuum. The set point temperature was reached in 80 s and annealing lasted 30 min.

Samples were measured at room temperature using a rotating polarizer ellipsometer. The usual spectral range used was from 1.4 to 5 eV. For the thinnest films the region between 0.7 and 1.4 eV was also covered. The spectra were analyzed with a 5-phase

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(ambient/SiO_2/film: unknown/SiO_2/Si substrate) multilayer model. To obtain all layer thicknesses for every sample, the dielectric functions of the Si substrate and of the SiO_2 were fixed to reference values [5,6]. The Ge films were treated as unknowns and their dielectric functions were parameterized using splines as previously described [7]. This general parameterization is very useful to fit layer thicknesses in the same way for all samples, without having to introduce different explicit models for the Ge layers. Obtained oxide thicknesses were around 15 nm (cap layers) and 100 nm (buffer layers), and Ge thicknesses were confirmed to be around nominal values. Besides, this analysis showed that changes in the spectral characteristics of the raw spectra are mainly due to variations of the Ge films. In particular, the evolution of the dielectric functions for increasing annealing temperature indicates a change from a fully amorphous layer to an amorphous Ge matrix with Ge crystallites, and eventually a fully crystallized Ge film. Once the layer thicknesses are known, more accurate dielectric functions have been obtained from energy-by-energy numerical inversion.

Transmission electron microscopy (TEM) was used to obtain structural information. The samples were investigated by an analytical transmission electron microscope JEOL 3010 at 300 keV. Specific polishing and thinning procedures using lubricants without water were employed to minimize sample oxidation. Final thinning to electron transparency was achieved by milling from one side using a low energy ion mill GentleMill from Technoorg. The samples were cooled during thinning.

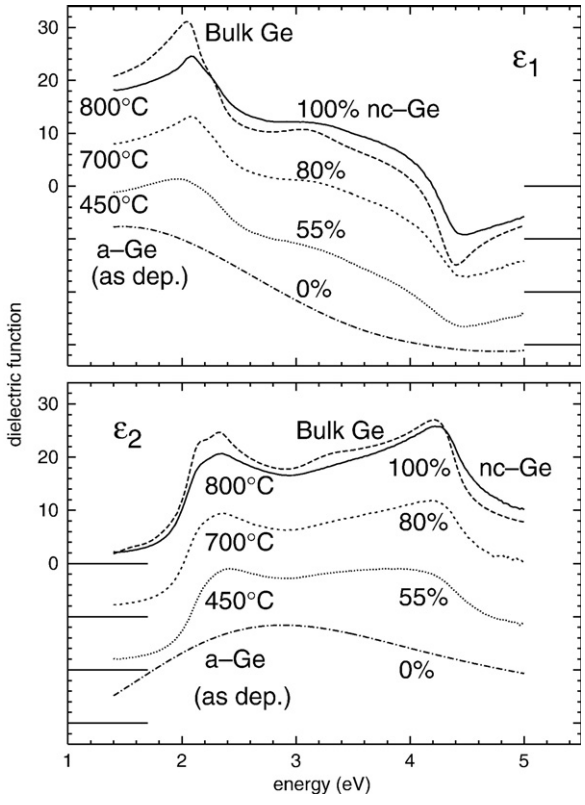

Fig. 1. Dielectric functions of some 50 nm-thick Ge layers after annealing processes at different temperatures. The vertical scales are for the upper curves and the rest are displaced as indicated. We observe the evolution from amorphous to nanocrystalline Ge (nc-Ge). Intermediate spectra are well described by effective mixtures of them, with the amount of crystalline material given in the labels.

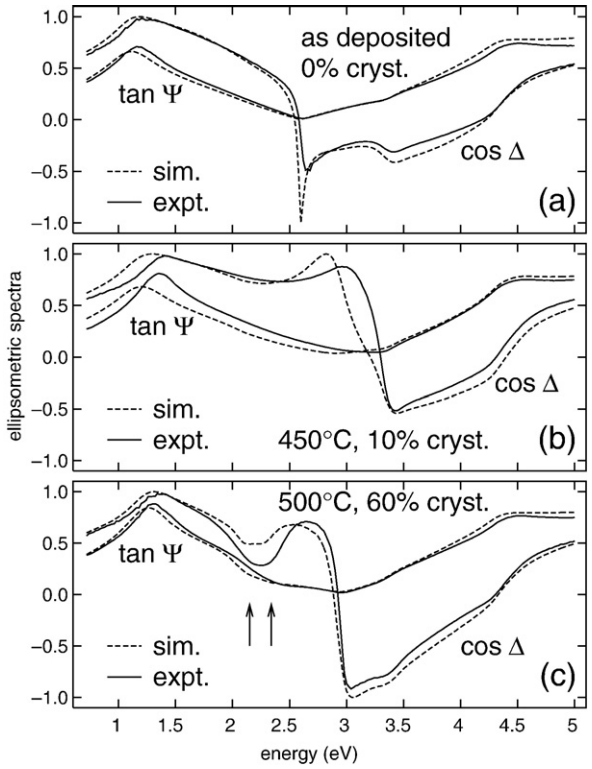

Fig. 2. Experimental and calculated tanΨ and cosΔ spectra for three representative samples with 10 nm-thick Ge films showing the onset of crystallization. The spectral feature that develops between 2 and 3 eV is due to E_1 and $E_1+\Delta_1$ interband transitions, whose energies for (c) $T=500$ °C are marked by arrows.

3. Results and discussion

An example of the evolution of ellipsometric spectra is shown for several 50 nm-thick Ge films in Fig. 1. The spectrum of the as-deposited film closely coincides with that of amorphous Ge [8]. With increasing annealing temperature clear spectral features due to E_1 (~2.2 eV) and E_2 (~4.2 eV) interband transitions appear [9]. In fact, the dielectric functions shown in Fig. 1 can be regarded as effective values. Then, volume fractions of amorphous and crystallized material can be evaluated by applying the Bruggeman effective medium approximation [10]. Notice that the largest difference in absolute values of ε between *a*-Ge and c-Ge occurs around the E_2 critical point. Therefore, this spectral region is most sensitive to the *a*-Ge/c-Ge composition. Accordingly, the sample annealed at 800 °C contains a totally crystallized Ge film. However, the obtained ε differs from a reference measurement on bulk Ge, also plotted in Fig. 1. At first sight, the largest difference is a reduced intensity of the E_1 transitions, which is correlated to the nanocrystalline structure of the Ge layer [11–14]. To determine the volume fractions of crystallized and amorphous Ge in every sample it is necessary to use as input the characteristic ε of the components. Using the ε measured on bulk Ge as c-Ge reference we cannot reproduce well the experimental spectra. On the contrary, using the