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Stability and transport properties of microcrystalline $Si_{1-x}Ge_x$ films

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Abstract

The crystallization evolution of boron and phosphorus doped amorphous $Si_{1-x}Ge_x$ films (5×10^{17}–5×10^{20} cm^{-3}), deposited on SiO_2/Si(001) substrates by molecular beam in high vacuum at room temperature, were studied by XRD, TEM and SEM. The amorphous $Si_{1-x}Ge_x$ films were fully crystallized at ~600°C. Up to 800°C no morphology changes were observed. Between 800 and 950°C, voids and hillocks were gradually developed in the films, which consequently collapsed. The Hall concentration and mobility were characterized in the $Si_{1-x}Ge_x$ films, annealed between 600 and 800°C. The mobility and conductivity of p-$Si_{0.5}Ge_{0.5}$ films at room temperature were found to be relative high: 60 cm^2/V s and 2000 $(\Omega\ cm)^{-1}$, respectively.

Keywords: Silicon–germanium films; X-ray diffraction; Crystallization; Hillocks; Electron transport

1. Introduction

Polycrystalline $Si_{1-x}Ge_x$ films have a variety of applications in semiconductor-on-insulator technology [1,2] as TFTs for AMLCD due to their high carrier mobility, high electrical activation of dopants [3] and low thermal budget [1]. In addition, the bandgap of poly-$Si_{1-x}Ge_x$ films can be regulated (via x), which is important for CMOS transistor gates [4,5] as well as for solar cells [6].

Solid-phase crystallization (SPC) from amorphous phase is the preferable process for producing polycrystalline $Si_{1-x}Ge_x$ film because of its ability to obtain structure with a desirable amorphous-to-crystalline ratio and a regulated grain size. As-deposited a-films are also not as rough as polycrystalline ones deposited by CVD, which is important for devices with increased channel carrier mobility [7].

However, SPC in $Si_{1-x}Ge_x$ films have not been studied in detail as undoped and doped Si-films [8,9]. It is interesting to note that relatively high doping (0.1–1%) of B, P and As strongly inhibits crystallization, while low doping (10–100 ppm) of the same impurities stimulates crystallization of a-Si.

Some studies of SPC in hydrogenated a-$Si_{1-x}Ge_x$:H(x = 0–1), undoped and highly doped with B or P, were recently carried out and demonstrated a strong influence of doping on crystallization parameters [10].

The main purpose of this research was to study systematically the crystallization process of a-$Si_{1-x}Ge_x$ films having various Ge content (x) and dopings (of B or P), and in addition, to characterize transport properties of crystallized films and to correlate these properties to the microstructure of the $Si_{1-x}Ge_x$ films. We studied also a disintegration process in $Si_{1-x}Ge_x$ films which is typical for semiconductor-on-insulator (SOI) systems at high temperatures, limiting an upper temperature limit of thermal treatment in the SOI. This process was investigated earlier in detail only in Si-films on SiO_2 and Si_3N_4 substrates [11].

2. Experimental

Amorphous $Si_{1-x}Ge_x$ films, 0.2 μm thick, undoped and doped by boron or phosphorus, were deposited at room temperature by molecular beam in ultrahigh vacuum (~10^{-10} Torr) on SiO_2(1000 Å)/Si(001) substrates. The films were deposited with various Ge contents x = 0–1. Some of the films were doped with B in concentrations of 5×10^{18}, 5×10^{19}, and 5×10^{20} cm^{-3} or with P (1×10^{20} cm^{-3}). The amorphous $Si_{1-x}Ge_x$ films were crystallized by vacuum annealing at temperatures between 500 and 900°C for 15 min to 10 h. In-situ XRD experiments were carried out using synchrotron radiation at the ESRF, Grenoble, France. In-situ transmission electron microscopy (TEM) studies were conducted in order to study the nucleation

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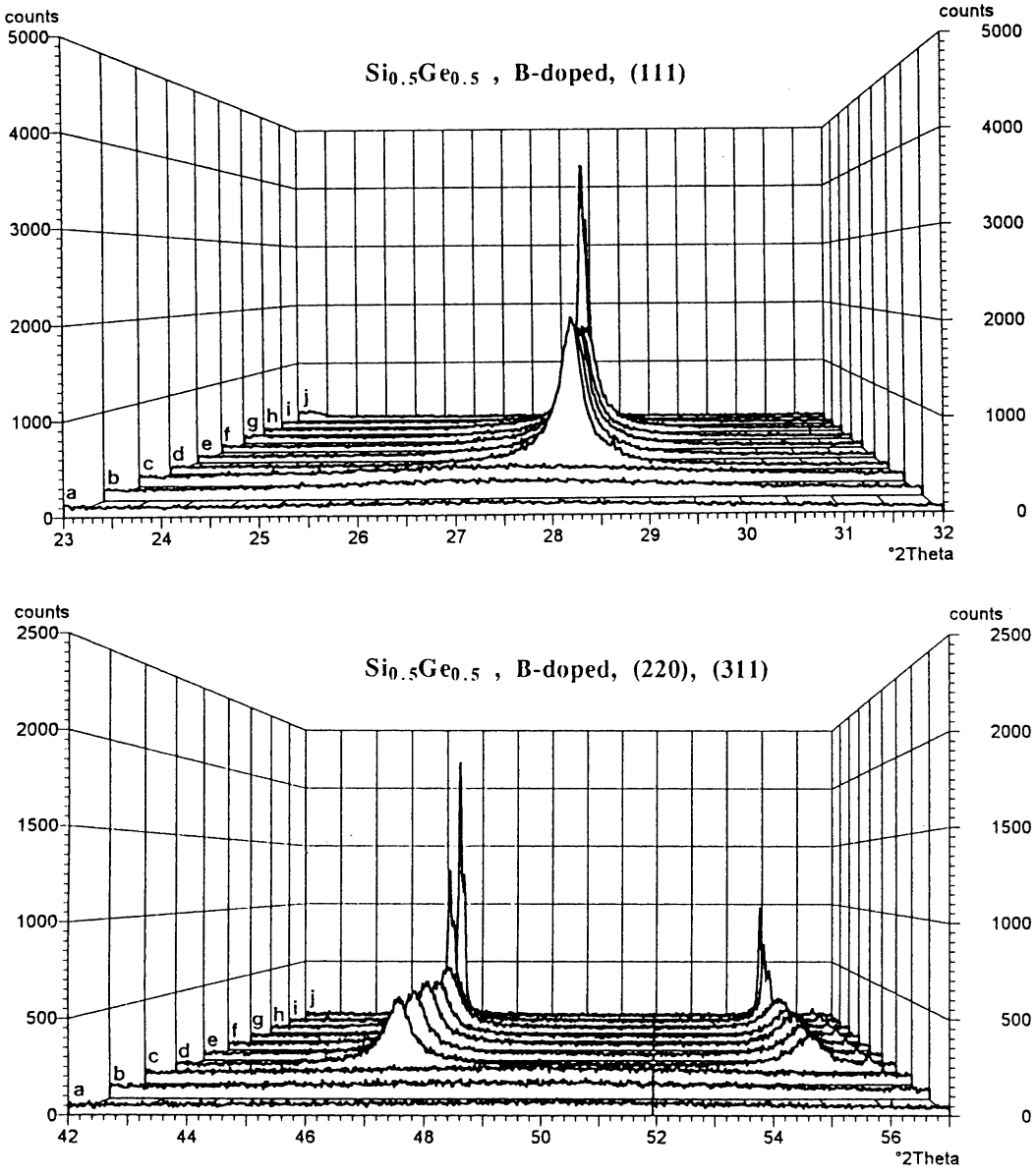

Fig. 1. XRD (111), (220) and (311) spectra of $Si_{0.5}Ge_{0.5}$ B-doped films. (a) As-deposited state and after 1 h annealing at: 500°C (b), 550°C (c), 600°C (d), 650°C (e), 700°C (f), 750°C (g), 80°C (h), 850°C (I) and 900°C (j).

and grain growth stages at low temperatures (500–600°C). The crystalline SiGe films morphology was studied using scanning electron microscopy (SEM). The Hall concentration (p_H), mobility of the holes (μ_H), and electrical conductivity, σ, were measured as a function of temperature in the range 85–380 K.

3. Results and discussion

3.1. Crystallization of amorphous SiGe films

XRD spectra of B-doped a-$Si_{0.5}Ge_{0.5}$ films annealed at 600–900°C for 1 h are shown in Fig. 1. Crystallization starts at 600°C, and no preferred orientation was observed. After $T \geq 850$°C SiGe films were recrystallized.

The dependence of the crystalline fraction f(t) in undoped and B- or P-doped $Si_{0.5}Ge_{0.5}$ versus annealing time (Fig. 2) was obtained by using in situ XRD. It was found to follow Avrami sygmoida [12]

$$f(t) = 1 - \exp\{-[(t - t_0)/\tau]\}^n \quad (1)$$

where $3 \leq n \leq 4$ for 3D and $2 \leq n \leq 3$ for the 2D case. τ is the characteristic time of the crystallization process (transformation of 63%) and is given by

$$\tau = \left[\pi/3\left(N v_g^{\,3}\right)\right]^{-1/4} \quad \text{(for the 3D case)} \quad (2a)$$

and

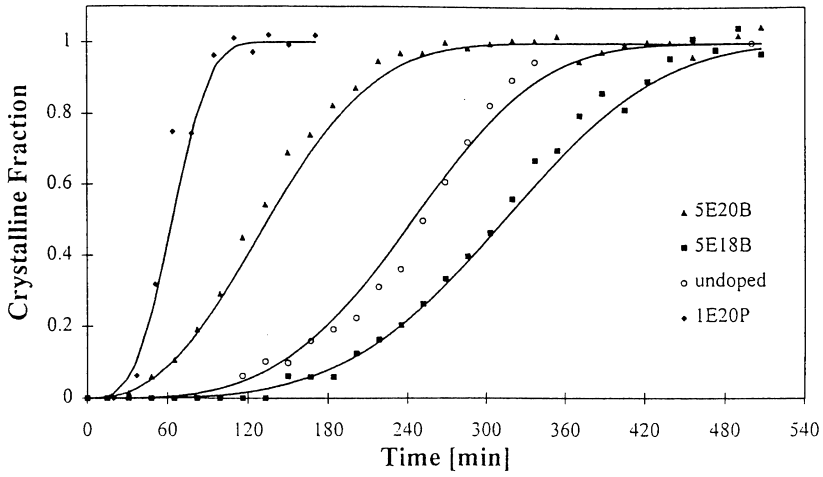

Fig. 2. The time dependence of the crystallization fraction *f*(t) deduced from the integral intensity of the (220) peak for undoped, B- and P-doped films at 550°C (in situ synchrotron radiation XRD).

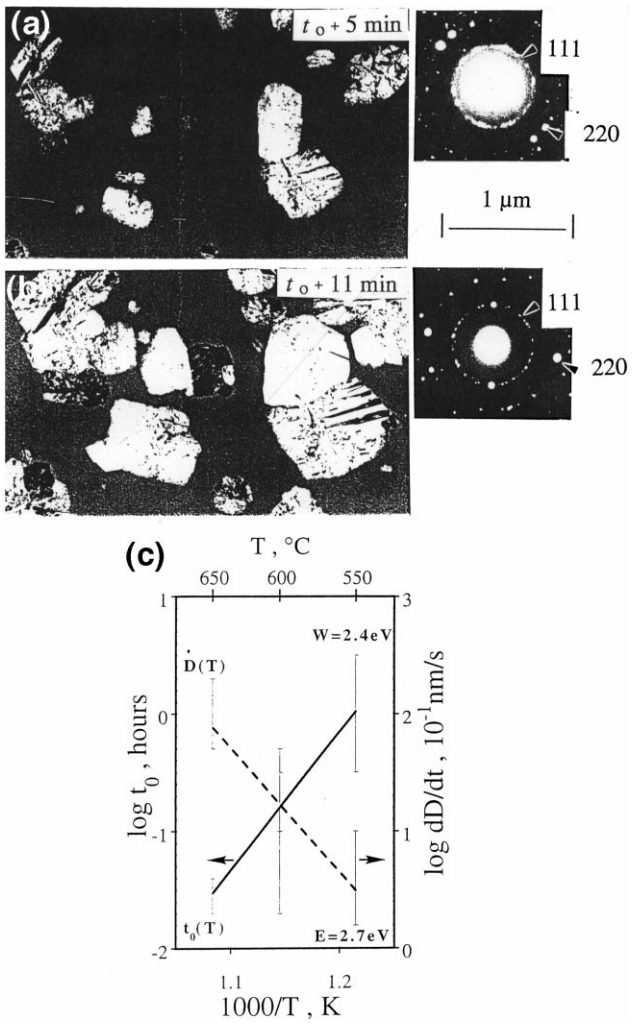

Fig. 3. In situ TEM crystallization in undoped $Si_{0.5}Ge_{0.5}$ film annealed at 600°C. Micrographs of the same area after t_0 + 5 min (a) and t_0 + 11 min (b); t_0 = 6 min. (c) Temperature dependence of the incubation time, t_0 and the grain growth rate d*D*/dt (*D* is a grain size), based on in situ TEM data.

$$\tau = \left[\pi/3\left(N v_g^{\,2}\right)\right]^{-1/3} \quad \text{(for the 2D case)} \tag{2b}$$

where N is the nucleation rate, v_g is the grain growth rate and d the film thickness. $N = N_0 exp(-H/kT)$ and $v_g = v_{g0}\exp(-E/kT)$, where H and E are the activation energies of nucleation and of grain growth, respectively. The temperature dependence of the incubation time is $t_0 = t_0$*exp(W/kT), where W is the overall activation energy of crystallization. The crystallization time, τ, decreases in undoped $Si_{0.5}Ge_{0.5}$ films from ~270 min at 550°C to ~16 min at 600°C, owing to an increase of N and v_g with increasing temperature. When N is high and v_g low, as was observed earlier in SiGe:H:B films [10] and SiGe:Ga [13], the crystallization results in nanocrystalline structure and $n = 4$ at any crystallization temperature and film thicknesses, a clear 3D-mode.

v_g, N and the incubation time t_0, in undoped and B-doped a-$Si_{0.5}Ge_{0.5}$ films, were estimated directly in our research by in situ TEM (Fig. 3). The measured values of N and v_g were 3×10^{10} cm^{-3}/s and 10 Å/s at 600°C, respectively. It was found that v_g is independent of time at a certain temperature. Such measurements were done at 550–650°C and the temperature dependencies of t_o and v_g allow us to estimate the activation energies for the overall crystallization, W = 2.4 eV, and for the grain growth, E = 2.7 eV. These values are of the order of the values obtained in the literature for Si (W = 2.75–3.9 eV, E = 2.6–2.7 eV [9]) and Ge (W = 2 eV [14]).

The in situ TEM study of highly B-doped $Si_{0.5}Ge_{0.5}$ film ($B = 5 \times 10^{20}$ cm^{-3}) at temperatures between 550 and 650°C showed that v_g is ten times larger than that in undoped film. This result is in accordance with the results obtained by in situ XRD.

3.2. Transport properties of B-doped $Si_{1-x}Ge_x$ films

Transport properties were measured in polycrystalline B-

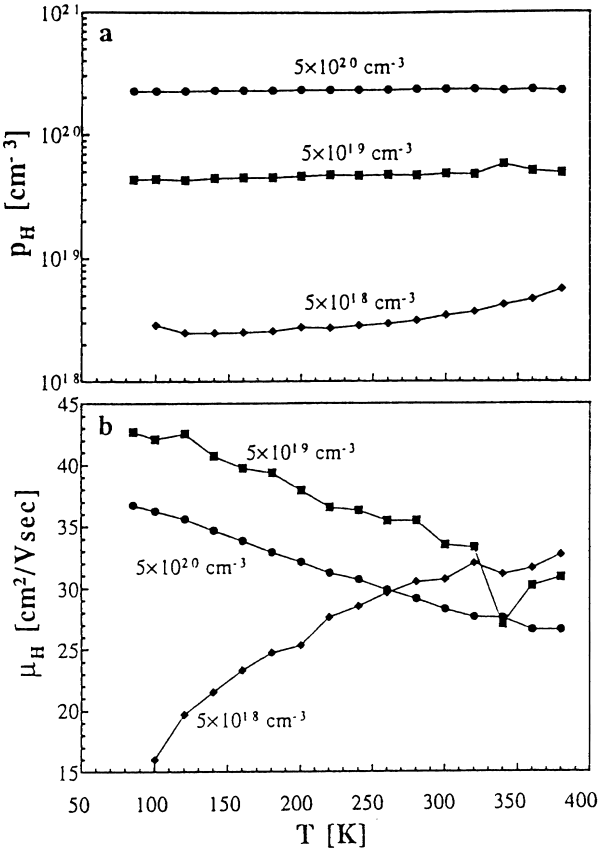

Fig. 4. Transport properties of B-doped (5×10^{18}, 5×10^{19} or 5×10^{20} cm^{-3}) $Si_{0.5}Ge_{0.5}$ after 600°C/1 h annealing. (a) Hall hole concentration (p_H) and (b) Hall hole mobility (μ).

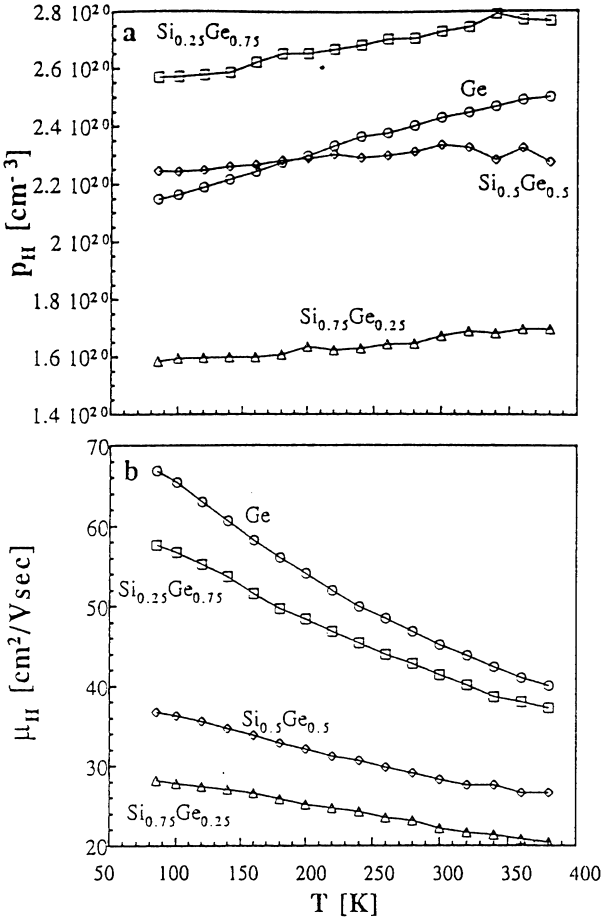

Fig. 5. Transport properties of B-doped (5×10^{20} cm^{-3}) $Si_{1-x}Ge_x$ for $x = 0.25, 0.5, 0.75$ and $x = 1$ after 600°C/1 h annealing. (a) Hall hole concentration (p_H) and (b) Hall hole mobility (μ).

doped (5×10^{18}, 5×10^{19} and 5×10^{20} cm^{-3}) $Si_{1-x}Ge_x$ films ($x = 0, 0.25, 0.5, 0.75$ and 1), which were crystallized during annealing at temperatures between 600 and 800°C

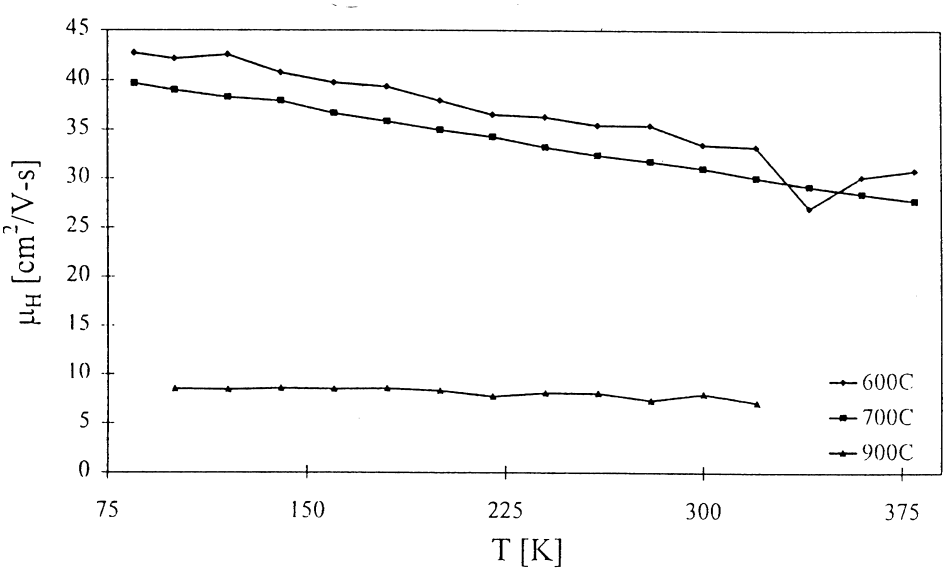

Fig. 6. Hole mobility in $Si_{0.5}Ge_{0.5}$ films annealed at different temperatures.

for 1 h (Fig. 4 and Fig. 5) when the films are stable. The Hall hole concentration is independent of the temperature of measurement in the range of 85–380 K. This is a typical behavior of degenerated semiconductors, known for bulk samples Si and Ge [15,16]. The Hall hole concentration was always smaller than the impurity concentration. This incomplete boron electrical activation probably results from segregation to interstitial sites (non-active position) since no precipitation could be resolved by TEM. The electrical activation of B was found to depend both on its chemical concentration and on the Ge content in the $Si_{1-x}Ge_x$ films (with maximum for $x = 0.75$). The activation dependence on the B doping level shows a maximum at $[B] = 5 \times 10^{19}$ cm^{-3}.

The Hall hole mobility for highly B-doped (5×10^{19} and 5×10^{20} cm^{-3}) $Si_{1-x}Ge_x$ films decreases with increasing temperature. This behavior is also expected [15,16], because at $T > 100$ K carriers scatter predominantly by acoustic phonons ($\mu \sim T^{-1.5}$). It is very important to mention that the microcrystalline p-$Si_{1-x}Ge_x$ films developed in this study are characterized by high room temperature mobilities (up to 45 cm^2/V s) values, that are close to the maximum one obtained in highly-doped ($[B] = 5 \times 10^{19}$ cm^{-3}) monocrystalline Si (50–60 cm^2/V s, [15,16] and large-grain SiGe materials (30–90 cm^2/V s [17,18]). It was also found that the Hall mobility of $Si_{1-x}Ge_x$ increased with the Ge content and subsequently, the electrical conductivity as well.

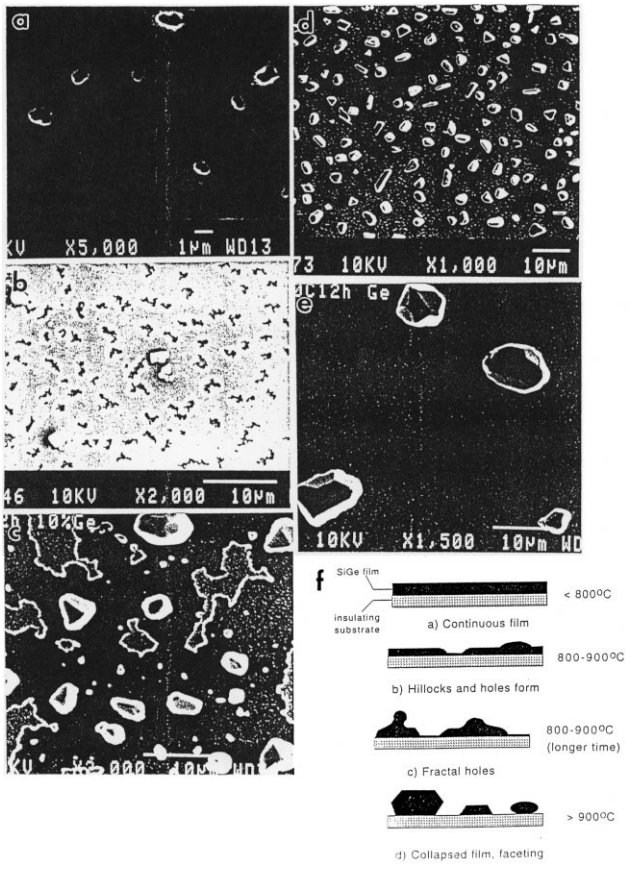

Fig. 7. Hillocks and pores in 0.2 μm thick undoped $Si_{1-x}Ge_x$ films on SiO_2/Si substrates after annealing at 800–900°C (SEM). (a) Si 800°C/1 h, (b) Si 800°C/10 h, (c) $Si_{0.9}Ge_{0.1}$, 900°C/12 h, (d) Ge 900°C/6 min, (e) Ge 900°C/12 h, (f) schematic picture of hillock growth.

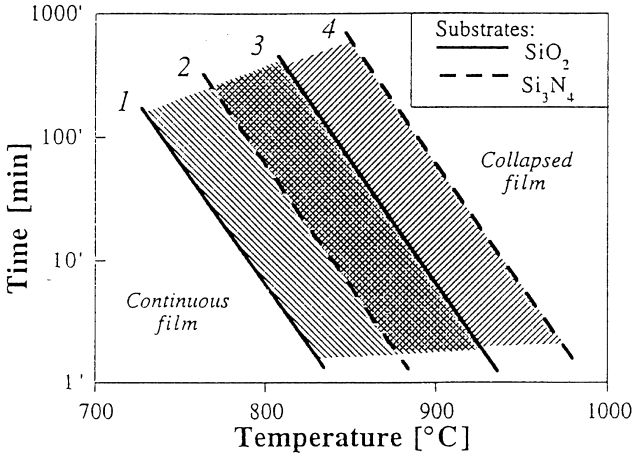

Fig. 8. *T*/t area of hillock formation in $Si_{0.5}Ge_{0.5}$ films on SiO_2 and Si_3N_4substrates.

3.3. Hillocks in SiGe films

The SiGe films annealed at 900°C demonstrated bad transport properties (see mobility in Fig. 6). The morphology was studied in Si, Ge, and $Si_{0.5}Ge_{0.5}$ films, 0.2 μm thick, at 800, 850, 900 and 950°C for 0.1, 1, 10 and 12 h. Fig. 7 shows the evolution of film collapse with temperature increase: (a) at ~800°C single holes formed (hole size is larger than grain size); (b) single holes collected in fractal pores; (c) upper film sublayer forms hillocks, but the layer in contact to substrate still exist; (d) pseudodrops and facetted microcrystals cover SiO_2 or Si_3N_4 substrate, film is totally desintegrated, it should be non-conductive; (e) material redistributed via surface diffusion to large crystals (10–100 times larger than the film initial thickness, see schematic Fig. 7f). Fig. 7e demonstrates that dominant faceting develops via (111) cuboctahedral planes which are the most stable in diamond-like Si–Ge lattice having maximum surface energy. Similar results were reported for poly-Si films deposited by LPCVD over SiO_2 or Si_3N_4 substrates [11]. The resulting diagram of the undoped $Si_{0.5}Ge_{0.5}$ film is presented in Fig. 8. We found also that high doping by boron (5×10^{18}–5×10^{20} cm^{-3}) decreased the trend of the film to hillock formation, probably, because the atoms of boron hinder surface self-diffusion of Si and Ge in SiGe film.

4. Conclusions

1. The crystallization process of amorphous $Si_{1-x}Ge_x$ films follows Avrami kinetics and results in microcrystalline structure.

2. Annealing conditions were established to obtain in future a desired amorphous to crystalline ratio in undoped, B- and P-doped $Si_{1-x}Ge_x$ films.
3. The $Si_{1-x}Ge_x$ films demonstrated Hall mobility of 25–45 cm^2/V s and electrical conductivity of 200–2000 $(\Omega\ cm)^{-1}$ at room temperature. The value of the mobility is close to the maximum one obtained in highly doped monocrystalline Si or Ge.
4. Morphological transformations in SiGe films on SiO_2 and Si_3N_4 substrates (pores, hillocks) lead to disintegration of the films starting at $T \geq 800$–850°C

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