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Evolution and control of the structure of a SiO_2/semiconductor nanoelectronics material

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Abstract

The study of a silica nanolayer implanted by semiconductor (germanium or silicon) species offers unique insights regarding the structural evolution and, ultimately, the controlled fabrication of nanoelectronics multiphase materials through one or more phase transformation steps. A description integrating important restructuring phenomena identified so far is provided and special emphasis is placed upon the interpretation and consequences of new transmission electron microscopy observations of in situ phase separation of Ge-implanted nanolayers.

Keywords: Phase separation; Glass transition; Nanocrystals; Electron irradiation; Silica; Nanolayer

1. Introduction

Nanoelectronics devices often involve active layers made of novel materials. The novelty may pertain either to the chemical nature of the material or its properly tailored nanostructure. In the latter case, the material often includes a minimum of two phases and the controlled phase separation, coarsening and crystallization of a glassy single-phase precursor offers an attractive way to generate a nanostructure of the desired kind. In this work, pertinent insights gained from our continuing studies [1–4] of various aspects of the behavior of a semiconductor-implanted silica nanolayer will be integrated and extended to include the effects of electron irradiation. The typical starting single-phase material for our studies is a $\approx$10-nm thick SiO_2 nanolayer grown on a silicon wafer and implanted with very low energy Ge (3 keV) or Si (1 keV) ions at doses in the 1×10^{16} cm^{-2} range. Upon implantation, the semiconductor species are found predominantly within a 3–5-nm thick 'middle'

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band of the silica nanolayer. Upon annealing, the silicon and germanium implanted nanolayers behave quite differently. In the case of Si implantation, annealing induces phase separation and the structure can be controlled by a proper choice of the implanted dose and the annealing time and temperature [2,3]. In the case of Ge implantation, annealing leads to substantial losses of the implanted species but phase separation can still be induced by e-irradiation (see below). Parallel studies [1,4] allow for a correlation of structural features and electrical properties of the materials in discussion.

2. Phase transformation considerations

Free energy considerations suggest that the spinodal decomposition (SD) separation mechanism can generate phases having the same (or closely related) symmetry as the parent phase [5], while there are no symmetry restrictions in the case the nucleation and growth (NG) separation mechanism operates. Still, even in the case of SD separation one of the new phases can change its symmetry by a subsequent transformation (e.g. crystallization) to another phase. In the case of interest the starting material is amorphous. Hence, NG may directly lead either to amorphous or crystalline semiconductor domains, while SD cannot yield directly semiconductor (nano-)crystallites, but the latter may form after a subsequent crystallization step.

The amorphous starting material is a glass. Due to the presence of a variation in composition in the thickness (z) direction, the material may be approximated as a system of three near-'single phase' nanolayers ('bands'), of which the middle one is more prone to restructuring as a result of its reduced glass transition temperature. For simplicity, the phase diagram shown in Fig. 1 includes only the binodal phase boundary, which is the one immediately experienced by the initial, amorphous and single-phase, semiconductor–SiO_2 nanolayer. Still, it is understood that in case semiconductor crystallization is possible, a monotectic point (and corresponding additional phase boundaries) need to

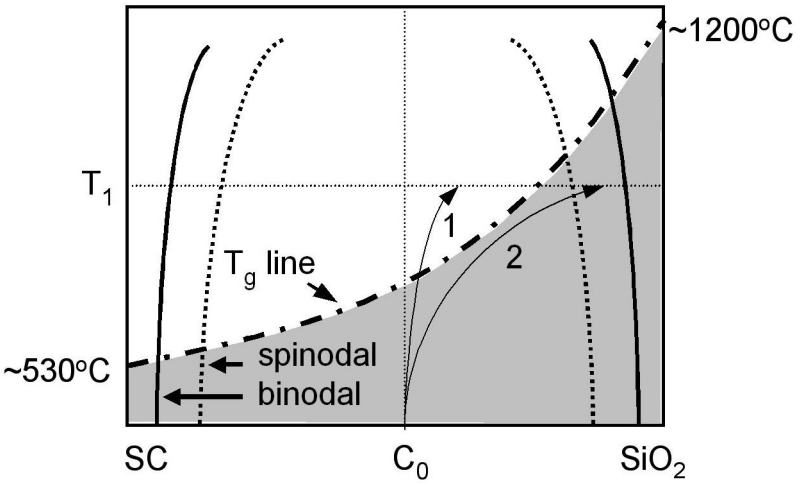

Fig. 1. Schematic phase diagram (binodal only) for a silica (SiO_2)–semiconductor (SC) system. The glass transition (T_g) line is included (grey area: single-phase glass). C_o: starting composition. The (1) is an example of a compositional path during the annealing of a Si-implanted sample, while (2) is the corresponding case for a Ge-implanted sample. T_1: annealing temperature.

be included. The starting compositions indicated in Fig. 1 pertain to the *middle* band while the other two bands are close to the 100% silica boundary. The glass transition line (T_g line, Fig. 1) is the locus of points having as coordinates single-phase compositions and their corresponding glass transition temperatures. T_g line is approximately drawn as described earlier [2]. For a single-phase composition inside the binodal it is kinetically necessary to surpass the glass transition line in order for phase separation to occur at appreciable rates [6]. Glass transition line will also impose limitations on the composition and the relative amounts of the phases to form. The phase amount most affected by the presence of the T_g line is that of the semiconductor-rich phase; this follows from simple (phase diagram) + (T_g line) considerations and has been amply verified for the Si case [2]. If one of the phases to form upon phase separation is glassy and continuous (for the case of interest this is possible for the silica-rich phase), spatial restrictions will be imposed on the coarsening of the biphasic structure; this issue is currently explored in detail [7]. We note in passing that more precise considerations require inclusion of the effect of domain size [6,7] on the glass transition temperature (and also on the melting point, when crystallization is possible).

As the glass transition temperature of the starting glass is *much* lower in the middle band (where the semiconductor content is high), it is also possible to select annealing conditions such that the SiO_2-rich separation-derived phase will not impose any restrictions on coarsening, while the top and bottom bands will remain glassy and non-separated. In the latter case, the separating nanolayer will be sandwiched between two glassy bands and the latter will impose a new type of restrictions on the coarsening of the evolving middle-band biphasic structure. As a result, coarsening semiconductor nanocrystalline domains may adopt platelet shapes other than those minimizing surface free energy and an example for Si-nanocrystallites has already been presented and interpreted [3].

Annealing favors phase separation, as the T_g line can be surpassed by raising the temperature. On the other hand, annealing causes part of the semiconductor species to escape from the top (air–glass interface), a fact that leads to new middle-band compositions with higher glass transition temperatures. We find experimentally that the outcome of this interplay depends on the implanted species; the silicon-implanted glassy middle band phase separates, while the corresponding germanium-implanted band remains single-phase, as a result of the faster loss of semiconductor species (Fig. 1).

In the case of the Ge-implanted material, phase separation can be induced by electron-irradiation, which leads to an effective lowering of the T_g line. This is clearly demonstrated in the case of transmission electron microscopy (TEM) observation of both annealed and non-annealed samples (see below). Non-annealed samples phase separate by the SD mechanism, while annealed samples separate by the NG mechanism. The difference in the phase separation mode is due to a compositional shift from the unstable regime to the silica-rich metastable regime of the miscibility gap, as Rutherford back-scattering (RBS) measurements indicate that $\approx 80\%$ of the implanted semiconductor species are lost after annealing at 950 °C for 30 min.

3. TEM observations and discussion

Upon TEM observation, annealed Ge-implanted samples undergo NG phase separation. The growing Ge-rich domains appear to be (nano-)crystalline from the start. The spatial patterns observed (Fig. 2a) exhibit features that are unique to the nanoscale. In particular, it is common to observe Ge-depleted white pockets exhibiting Ge-rich ‘dots’ (nanocrystallites) at their periphery, without a

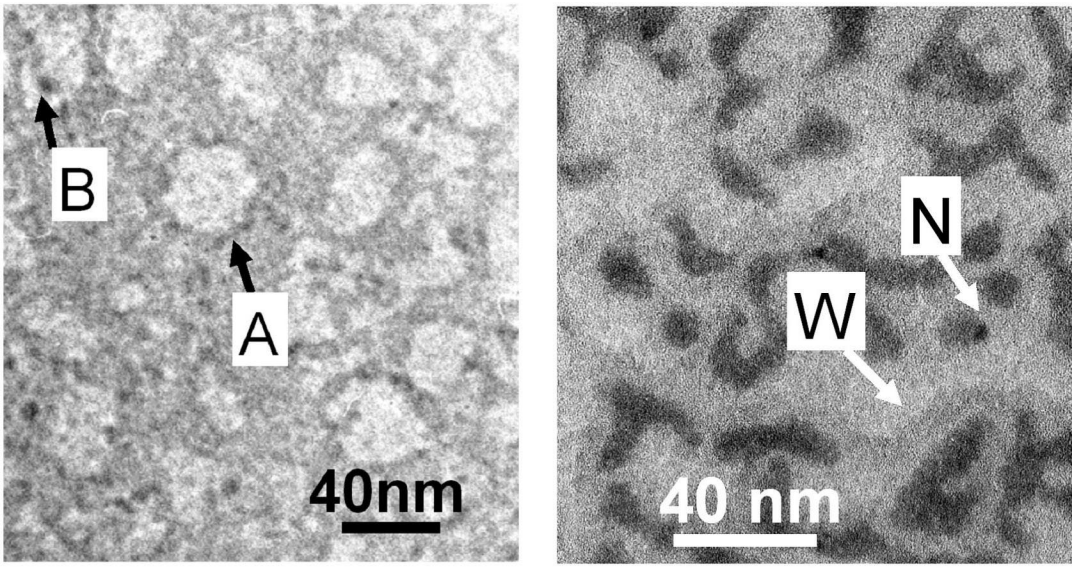

Fig. 2. Samples were Ge-implanted at a 1×10^{16} cm^{-2} dose. (a) Sample annealed to 950 °C for 30 min prior to TEM observation. Early stage of e-irradiation induced NG of Ge (black dots). Light areas: SiO_2-rich matrix. Grey areas: non-separated material. A and B: Different Ge nuclei configurations. (b) Non-annealed sample. Late stage of of e-irradiation induced SD. Ge-rich islands (dark grey) have undergone some degree of coarsening. Ge nanocrystals (N, black dots) also start to form by nanodomain-confined crystallization, while the light-colored SiO_2-rich areas undergo further separation and walls (W) indicate the location of the evolving additional compositional boundary.

Ge-rich 'dot' in the interior. Here, a depletion zone with a central dot, a configuration known to dominate NG structures phase-separated at larger scales, is less common. This peculiarity can be explained when the unusually high density of interfaces generated during nanoscale separation is taken into account. The total energy cost associated with the high density of interfaces is unfavorable for configuration B (Fig. 2a) and, as a result, configurations of the A type become common.

Fig. 2b offers a visual 'synopsis' of processes occurring in non-annealed samples upon TEM observation. The main phase separation mode is SD and leads to the dominant pattern of dark (amorphous Ge-rich) and light (amorphous SiO_2-rich) areas, both exhibiting curvature of alternating sign. Comparison with images obtained at earlier times (not shown) suggests that Fig. 2 captures a *partially*-coarsened SD structure. Closer inspection suggests that Fig. 2b contains evidence for a total of *three* phase transformations. In addition to the dominant SD pattern we observe walls (W) and Ge nanocrystals (N). The walls are the result of a further amorphous–amorphous (nano)phase separation which splits silica-rich matrix into silica-'very rich' and silica-'moderately rich' bands. The formation of Ge nanocrystals is also a *secondary* transformation process, as it takes place within the amorphous Ge-rich domains formed through SD. Interestingly, real time observations in the dark field mode allow for the observation of fine details of Ge nanocrystallization within the larger Ge-rich domains; in particular it is possible to observe both the growth of 'large' nanocrystalline embryos and the frequent formation and decay of smaller, subcritical nanocrystalline embryos.

By defocussing the electron beam, the described restructuring processes are found to freeze. It

follows that the Ge/SiO_2 nanolayer (and more generally a single-phase two-component glassy nanolayer) may be electron-beam patterned with the option of selecting the precise nanostructure, with the help of TEM observations as a function of time. Experimentation suggests that times typical for structures of interest to evolve under common TEM e-irradiation/observation conditions at 200 keV range from 10^{-1} to 10^{1} min. Furthermore, as, apart from the lowering of the effective T_g line, TEM observation leads to processes that can be understood without invoking special e-irradiation effects, it appears reasonably safe to view pertinent observations as a handy and unique guideline for nanostructuring processes achievable by annealing of a phase separating two-component glassy nanolayer.

Additional, preliminary observations on Ge-implanted samples annealed in the presence of a capping polysilicon layer suggest that the loss of Ge is reduced and, as a result, the sample is already separated at the beginning of the TEM observation. In the latter case the behavior of the Ge-implanted samples is expected to be comparable to that of the Si-implanted samples studied earlier and briefly outlined in parts of the previous section.

Ge-based work presented here, Si-based work presented in more detail earlier [2,3] and related work by other groups (e.g. Ref. [8]) make clear that a two-component single-phase glassy material having one nanodimension offers a wide variety of nanostructuring options accessible though proper processing. Several important restructuring processes within a separable glassy nanolayer are currently understood in satisfactory detail, at least at the qualitative level; optimized processing is a challenging and, potentially, a highly rewarding pursuit.

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