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Surface-Energy-Driven Graphoepitaxy in Ultrathin Films of Ge

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Abstract

Solid-state, surface-energy-driven grain growth in ultrathin films of Ge (10-100 nm) confined with SiO_2, produces a predominance of (110) texture in secondary grains several μm in diameter. If the SiO_2 substrate is patterned with a 0.2 μm-period relief grating, 10 nm deep, the secondary grains have a predominance of (100) texture, and these grains show a graphoepitaxial orientation with <100> directions preferentially parallel and perpendicular to the grating axis. Patterning films into 1 μm-wide stripes enhances secondary grain growth over the gratings, and grains with (100) texture show a preferential in-plane orientation.

Introduction

Methods for producing crystalline films on amorphous substrates without any seeding, in which orientation is controlled by artificial patterning, have been investigated for a number of years.[1] In contrast to processes which involve melting and resolidification, processes based on solid-state grain growth[1-4] offer the possibility of operating at temperatures well below the melting point. Surface-energy-driven grain growth is a solid-state process in which grains which are oriented such that the sum of the free-energies of their top and bottom surfaces is minimum grow by consuming neighboring grains.[1-4] Since minimum surface free-energy will generally correspond to a specific crystallographic texture the resulting secondary grains should have a uniform texture (but random azimuthal orientations). The driving force for surface-energy-driven growth of secondary grains is inversely proportional to film thickness[3], and thus, ultrathin films are required.[1-4] In our investigation of Ge, films in the thickness range 10-100 nm have been investigated. In this paper we report that a surface-relief grating in the SiO_2 substrate, having 0.2μm period and approximately square-wave profile, induces in both patterned and unpatterned films of Ge the growth of grains with (100) texture and <100> directions preferentially parallel to the grating axis.

Experimental Details

Gratings of 0.2μm-period with square-wave profile were etched 10 nm-deep into 0.1μm-thick SiO_2 on (100) Si wafers using a combination of x-ray lithography and reactive-ion etching.[4] After careful cleaning of the substrates Ge was deposited at room temperature over the gratings to thicknesses in the range of 20-30nm by electron beam evaporation. A SiO_2 encapsulation layer, ~50-100 nm-thick, was deposited over the Ge by rf sputtering. In some cases, Ge films over gratings were patterned into ~1μm-wide stripes prior to encapsulation, using photolithography and chemical etching with H_2O_2:H_2O. The stripes were roughly parallel to the grating axis: <7°. Samples were cleaved into square pieces, ~2x2 mm, and inserted into fused silica ampoules. These were evacuated and then either backfilled with Ar and sealed, or sealed under vacuum using a torch. The sealed-off ampoules

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were then inserted into a furnace which was preheated to 900°C. Annealing times were 1, 2 and 16.5 hours (i.e., overnight). After removal from the furnace, samples were etched from the back side in a jet of $HF:HNO_3:H_2O$ up to the SiO_2 film underneath the Ge. In this way, the three-layer membrane, consisting of Ge sandwiched between layers of SiO_2, was suspended across a hole, about 100 µm diameter. This permitted the Ge grain structure and orientation to be analyzed in a transmission-electron microscope (TEM). The membranes always wrinkled after thinning due to compressive stress in the SiO_2.

Results and Discussion

When Ge films (<100 nm) on smooth SiO_2 substrates, without any encapsulation layer, are annealed at temperatures below melting (937°C) they agglomerate in the solid state into single-crystal beads.[2] In order to suppress agglomeration and obtain larger secondary grains we deposited the SiO_2 encapsulation layers over the Ge. Annealing of the encapsulated Ge films over 0.2 µm-period surface-relief gratings at 900°C for 1 hour causes individual secondary grains to grow to widths of up to ~1-2 µm and lengths along the grating axis of up to several micrometers. Figure 1 is a TEM micrograph of a secondary grain. (At the 16.5 hour annealing time, all normal grains are fully consumed and the film consists entirely of secondary grains several µm in size.) The inset electron diffraction pattern shows that the secondary grain has (100) texture with a ⟨100⟩ direction parallel to the grating axis. Figure 2 is a histogram of the distribution of in-plane orientations of the (100)-textured secondary grains, which includes results for all three annealing times. Note that the graphoepitaxy is not perfect, but clearly present. The grating in the SiO_2 was aligned roughly parallel to the [110] direction of the (100) Si substrate beneath the SiO_2. Thus, any influence of the single-crystal Si substrate on the Ge graphoepitaxy (e.g., through pinholes in the SiO_2) can be ruled out. The presence of a surface-relief grating strongly influences the texture of secondary grains. On smooth SiO_2 surfaces, the dominant (75%) texture is (110).[2] A (112) texture was observed in 25%

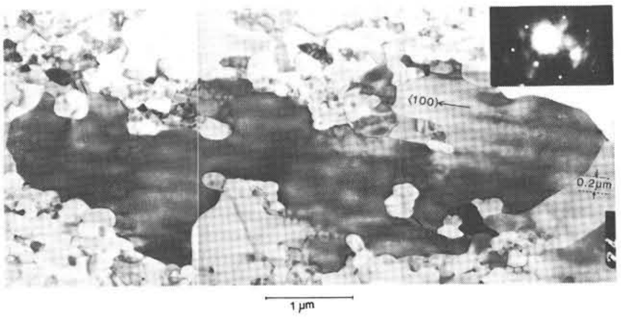

Fig. 1 TEM micrograph of secondary grain in 30 nm-thick Ge film over 0.2 µm-period surface-relief grating in SiO_2, with encapsulation of SiO_2, after annealing for 1 hour at 900°C. Grating depth is ~10 nm. The inset diffraction pattern indicates that the grain has (100) crystallographic texture and ⟨100⟩ direction parallel to the grating axis within a few degrees. The dotted line indicates the grating period and direction. With additional annealing time, the secondary grain would fully consume the normal grains surrounding it and included within it.

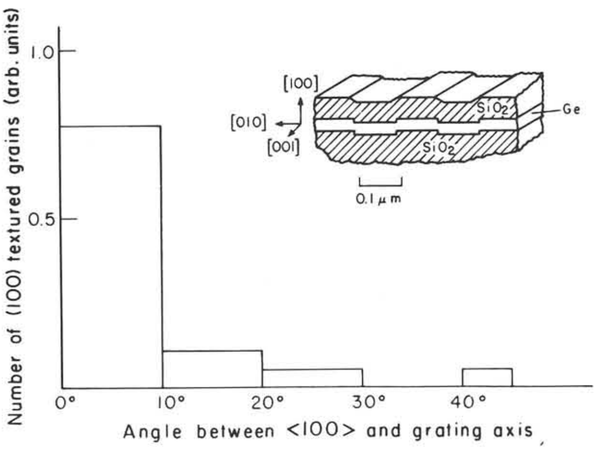

Fig. 2 Histogram of the in-plane orientations of thirty-eight (100)-textured secondary grains obtained in 30 nm-thick Ge films over 0.2 µm-period surface-relief gratings in SiO_2. Annealing was carried out at 900°C for 1, 2 and 16.5 hours. Thirty of the secondary grains were oriented within 10° of the grating axis.

of the secondary grains, which is the same as the texture observed in secondary grains of unencapsulated Ge.[2] No (100)-textured secondary grain was observed over smooth SiO_2 surfaces. For encapsulated Ge films over surface-relief gratings, 38 out of 40 secondary grains had (100) texture. This texture switch, observed earlier[2], is confirmed with this additional data. Germanium films, 20 nm-thick, patterned into 1 μm-wide stripes on the grating substrate and encapsulated with SiO_2 were annealed under vacuum at 900°C for 1 and 2 hours. After 1 hour, secondary grains up to 3 μm-long were observed, but a significant fraction of the stripes consisted of normal grains. After 2 hours annealing, larger secondary grains, up to 12 μm long were obtained, and nearly all normal grains were consumed, as shown in Fig. 3. This predominance of secondary grains after two hours at 900°C was not observed in unpatterned films under the same annealing conditions. We are uncertain why this difference occurs. It may be due to changes in film stress or stress gradients as a result of patterning and encapsulation. Brueck, et al.[5], using Raman techniques, reported increased stress at the edge of Si stripes confined with SiO_2. The textures of secondary grains in the Ge stripes were 52% (100) and 48% (110). (The total number of secondary grains with interpretable diffration patterns was 46.) About half of the (100)-textured grains have ⟨100⟩ directions along the grating axis to within 10°, while no preferential in-plane orientation of (110)-textured grains was observed. Moreover, (100)-textured grains tend to grow longer than (110) grains: average lengths of (100)- and (110)-textured grains were ~4 μm and ~2 μm, respectively.

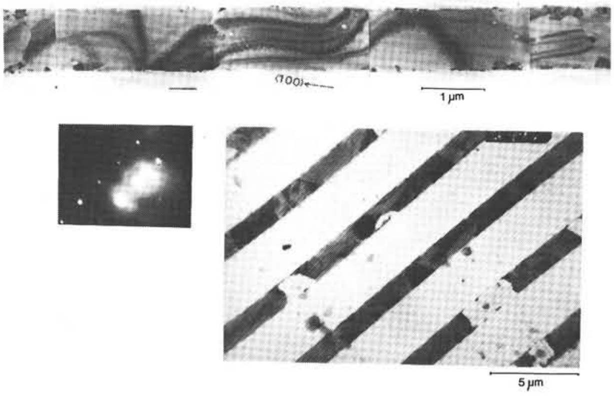

Fig. 3 TEM micrograph of 1 μm-wide stripes of 20 nm-thick Ge films over 0.2 μm period surface-relief grating, encapsulated with SiO_2. Annealing was done at 900°C for two hours. The lower micrograph (low magnification) shows stripes of Ge placed roughly parallel to the grating axis (~7° off) and the upper micrograph (higher magnification) indicates that the secondary-grain growth has resulted in a 12 μm-long secondary grain. Note a small number of normal grains are left in the vicinity where grain boundaries impinge against one another (at both ends of the micrograph). The inset diffraction pattern revealed that the large secondary grain is (100)-textured with a ⟨100⟩ direction along the grating axis to within a few degrees. The lower micrograph shows that agglomeration sometimes also occurs.

Conclusions

A surface-relief grating increases the interfacial area and hence the driving force for secondary grain growth and makes the surface artificially anisotropic, apparently favoring the growth of those (100) grains that have a ⟨100⟩ direction along the grating axis. These results are the first clear demonstration of graphoepitaxy resulting from solid-state surface-energy-driven grain growth. The secondary grain growth and solid-state graphoepitaxy reported here took place at a large fraction of the melting point. We believe it may be possible to reduce the temperature significantly by employing procedures that increase the surface-energy anisotropy or the grain boundary mobility, or both.

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