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 SiO₂, produces a predominance of (110) texture in secondary grains several μm in diameter. If the SiO₂ 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. In contrast to processes which involve melting and resolidification, processes based on solid-state grain growth 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. 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, and thus, ultrathin films are required. 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 SiO₂ 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 SiO₂ on (100) Si wafers using a combination of x-ray lithography and reactive-ion etching. 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 SiO₂ 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 H₂O₂:H₂O. 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 pre-
heated 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:HNO₃:H₂O up to the SiO₂
film underneath the Ge. In this way, the three-
layer membrane, consisting of Ge sandwiched be-
 tween layers of SiO₂, 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 SiO₂.

Results and Discussion

When Ge films (100 nm) on smooth SiO₂ sub-
strates, 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 agglomera-
tion and obtain larger secondary grains we
deposited the SiO₂ 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 pat-
tern 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 SiO₂ was
aligned roughly parallel to the [110] direction
of the (100) Si substrate beneath the SiO₂.

Thus, any influence of the single-crystal Si
substrate on the Ge graphoepitaxy (e.g., through
pinholes in the SiO₂) can be ruled out. The
presence of a surface-relief grating strongly
influences the texture of secondary grains. On
smooth SiO₂ surfaces, the dominant (75%) texture
is {110}.² A {112} texture was observed in 25%
of the secondary grains, which is the same as the texture observed in secondary grains of unencapsulated Ge. No (100)-textured secondary grain was observed over smooth SiO₂ surfaces. For encapsulated Ge films over surface-relief gratings, 38 out of 40 secondary grains had (100) texture. This texture switch, observed earlier, is confirmed with this additional data. Germanium films, 20 nm-thick, patterned into 1 µm-wide stripes on the grating substrate and encapsulated with SiO₂ 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., using Raman techniques, reported increased stress at the edge of Si stripes confined with SiO₂. The textures of secondary grains in the Ge stripes were 52% (100) and 48% (110). (The total number of secondary grains with interpretable diffraction 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.

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 graphopitaxy 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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