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Metastable phase formation in laser-processed Al–Ge sputtered thin films

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The formation of a metastable phase in $Al_{59}Ge_{41}$ thin films under microsecond laser irradiation is reported. Thin films prepared by co-sputtering are amorphous as-grown. Upon laser processing, amorphous and crystalline phases are detected and analysed using TEM and EDX. A metastable structure formed by laminar-textured aluminium alternating with an hexagonal metastable phase is observed.

1. Introduction

Rapid solidification processing techniques capable of producing 10^5 to 10^9 K sec^{-1} cooling rates are suitable to generate nonequilibrium structures and have been applied to the Al–Ge system [1–3]. Various metastable crystalline structures ranging from simple cubic to complex monoclinic [3–5] have been detected. In the case of submicron powders [3], three basic microstructures are observed depending on the undercooling rate. At low, medium and high cooling rates: a mixture of a metastable hexagonal phase and aluminium, a multicrystalline mixture of aluminium and germanium or a mixture of aluminium and amorphous phase are observed, respectively. The usual analysis techniques have been X-ray diffraction or transmission electron microscopy (TEM). Some discrepancies in the crystal lattice parameters have been observed, probably due to the small size of the products formed which need the use of microanalysis techniques.

Among other crystalline metastable phases the hexagonal phases are less observed and its relation to other phases is not clear at present [6]. The hexagonal phase ($a \simeq 1.35$ to 1.38 nm, $c \simeq 0.71$ to 0.72 nm) was first observed both in the material formed from the melted alloy [5] and in thin films grown in high vacuum upon electron-beam bombardment [7]. It was also detected in an eutectic laminar structure formed by the metastable phase and textured aluminium.

More recently, a hexagonal phase ($a \simeq 1.40$ to 1.42 nm, $c \simeq 0.72$ to 0.74 nm) has been observed in Al–Ge eutectic powders produced by electrohydrodynamic atomization, which were melted by means of electron-beam irradiation [8, 9]. The same authors again found a hexagonal phase in melt spun ribbons and in amorphous films crystallized by means of electron-beam irradiation [10], as well as in splat-quenched $Al_{63.5}Ge_{36.5}$ alloys [3].

The ion or laser interaction with Al–Ge compounds has been little studied, although it is known that ion-beam and laser mixing produces extended metastable solid solutions in systems where stable phases are not formed. An excellent mixing study of binary metal–semiconducting eutectic systems under ion irradiation and a comparison with laser irradiation results was performed by Lau *et al.* [11]: under ion irradiation a transformation of the Al–Ge layered structure was observed which could only be related to a solid-state reaction. A 15 nsec pulsed laser irradiation produced the melting and, consequently, the intermixing of the Ge/Al layers with the formation of an amorphous layer.

A more recent work [12] studied the laser mixing by means of excimer laser irradiation (12 nsec) of a Ge/Al multilayered structure with average compositions $Ge_{30}Al_{70}$ and $Ge_{40}Al_{60}$. The results have shown the formation of an amorphous layer with presumably eutectic composition when the layers mixed have that final average composition. In other cases the formation of both the amorphous eutectic layer and the segregation of germanium crystals at the interfaces were observed. Both investigations [11, 12] characterized the processed films structure by means of X-ray diffraction techniques. The germanium interface segregation [12] was analysed by means of cross-sectional TEM. No microanalysis techniques were used.

The present work will present a study of the structural transformations occurring in an $Al_{59}Ge_{41}$ thin film under laser irradiation. The pulse lengths used were 5 and 50 μsec. The morphology of the laminar metastable eutectic structures [3, 5, 13] formed by the hexagonal metastable crystalline phase and aluminium, as a function of the laser pulse length and the irradiation power will be discussed.

2. Experimental details

The amorphous thin films were grown on glass substrates in a co-sputtering triode system by means of two independently polarized Ge (99.99%) and Al

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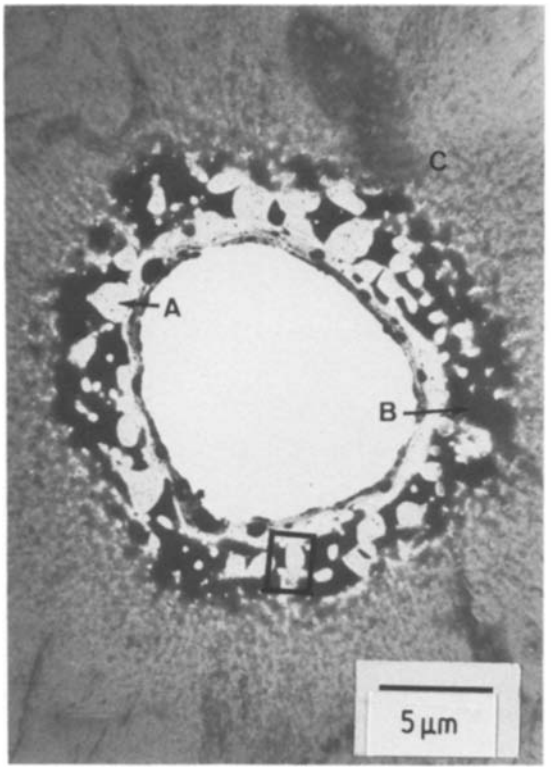

Figure 1 Example of the laser interaction of a 50 μsec pulse of 28 mW with the AlGe thin film. There is a central hole, surrounded by three areas with different structures: a residual amorphous film (A), the melted area (B) and the annealed area (C).

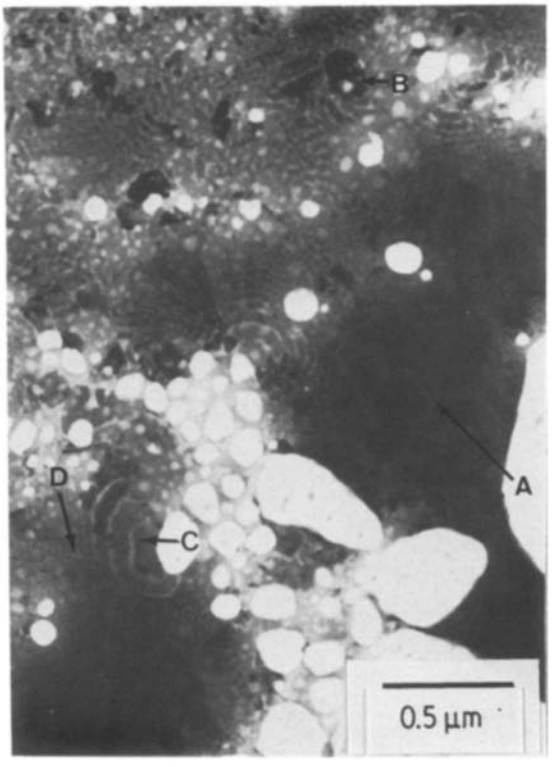

Figure 2 Magnification of the area marked in Fig. 1, with the following microstructures: (3 1 0) aluminium texture with some small germanium crystals (A), twinned germanium crystals (B) and metastable structure (C), (D).

(98%)–Si, Zn (2%) targets with growth rates close to 0.1 nm sec^{-1}. The film thickness was 35 nm. The residual pressure was 2.0×10^{-6} torr and the operating Argon pressure was 2.7×10^{-4} torr. The films were aged over 2 years in air and then floated in water to be supported in TEM grids for laser processing and analysis.

The thin film composition was determined by Rutherford backscattering (RBS) and the atomic content was $Al_{59}Ge_{41}$. In order to resolve the homogeneity of the films, depth profiling by means of Auger electron spectroscopy (AES) was performed. A high gradient of aluminium content was detected at the surface mainly in the form of Al_2O_3 while the germanium content increased its concentration near the substrate interface. The silicon content was uniformly distributed with depth.

The laser irradiation of films was carried out with an argon laser tuned to its 488 nm line and focused by mens of a 0.4 numerical aperture objective on the samples. The experimental conditions are similar to those described previously [14] and the exposure laser parameters were: 5 and 50 μsec pulse length and irradiation power in the 4 to 28 mW range.

The films were analysed by TEM and selected-area diffraction (SAD) in a Siemens Elmiskop 1A and a Philips EM-420. The last system was equipped with energy dispersive X-ray spectroscopy (EDX) (EDAX-9100) which analysed the material migration under laser processing. By means of SAD and bright- and dark-field images, we were able to study the crystallinity of the observed phases as well as the microstructures.

3. Results and discussion

The film presents a strong structural transformation under laser irradiation. Fig. 1 shows a transmission electron micrograph as an example of an area exposed to a 50 μsec and 28 mW laser pulse. A central hole is produced by an ablation process. Surrounding this hole three concentric areas are observed. The first (A in the figure) corresponds to areas very transparent to the electrons which are amorphous and mainly formed by aluminium as evidenced by SAD and EDX. The second area (B in Fig. 1) corresponds to the melted area. Its SAD patterns (SADP) correspond to an amorphous phase and several crystalline micro-structures. Because this melted area is where rapid solidification occurs, metastable phases are expected to be present. Finally, the outer part of Fig. 1 or the third area (C) refers to the film which has experienced a gentle annealing process caused by heat diffusion.

As the irradiation power is decreased, similar features are observed and the central hole tends to disappear (for 17 to 20 mW). At very low power exposures (< 8 mW) the melting area also disappears and only the annealed area is present in the centre of the irradiated area. When the exposure is reduced to 5 μsec, similar morphological and structural features are observed; nevertheless the melting and ablation thresholds are increased. A complete discussion of the behaviour of the structure and morphology as a function of the irradiation parameters will be reported elsewhere [15].

In Fig. 2, a magnification of the melted area corresponding to the area outlined in Fig. 1 is shown. A material richer in germanium than the as-grown film

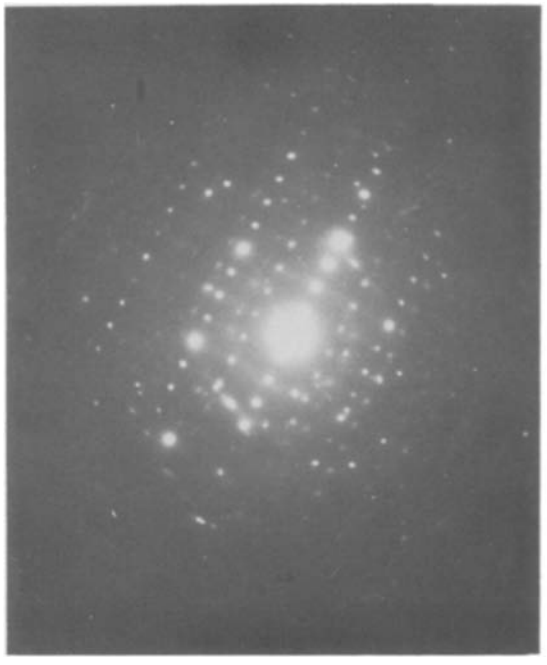

Figure 3 SADP of the central part of the metastable structure (concentric laminar structure), corresponding to a hexagonal (2 1 $\bar{3}$ 0) phase with aluminium overlapped.

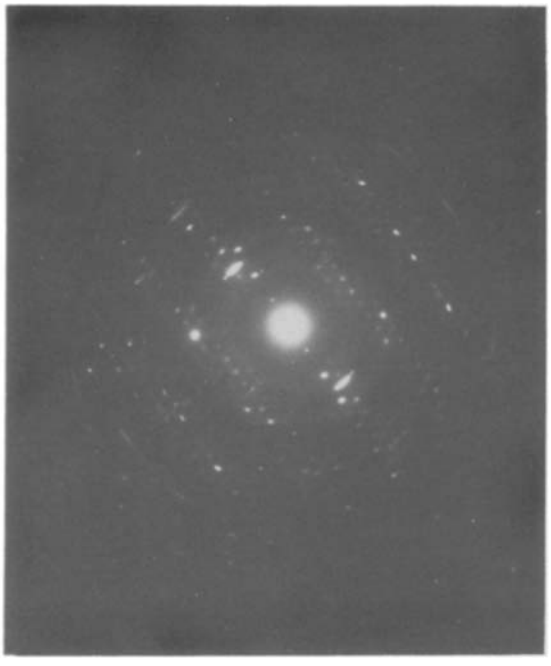

Figure 4 SADP of the outer part of the metastable structure (radial laminar structure), corresponding to the (0 0 0 1) reciprocal lattice plane of the hexagonal phase and the (2 1 1) aluminium texture.

is seen, where many voids have been produced. Two types of void, spheric and faceted are observed, the latter being similar to those previously observed in Al–Ge under ion irradiation [16].

Three different microstructures are basically differentiated in the melted area (Fig. 2). (a) Small germanium crystals (area A) which have grown randomly in a predominantly (3 1 0) aluminium texture matrix by a diffussion process similar to those of prior observations [5]. (b) Thin laminar twinned germanium crystals (area B). The typical size is 100 to 200 nm. (c) The metastable laminar eutectic structure [3, 5, 13], formed by a laminar aluminium crystalline matrix and a hexagonal phase (areas, C, D). The EDX analysis shows that this structure has the eutectic composition. This result supports the idea that the metastable hexagonal phase has a germanium composition richer than that corresponding to the eutectic one. The measured parameters for this hexagonal phase ($a \simeq$ 1.42 nm and $c \simeq 0.74$ nm) are in good agreement with previous determinations [8] or slightly higher [5].

Two different morphologies are observed for the metastable laminar structure: a central concentric structure (area C, Fig. 2) and an outer area with radial structure (area D, Fig. 2). Fig. 3 includes one of the typical SADPs of the former structure shown in area C of Fig. 2. These orthogonal patterns correspond to lattice planes parallel to the *c*-axis. The radial structure (area D of Fig. 2) is perpendicular to this first structure and presents the (0 0 0 1) diffraction pattern (Fig. 4) of the hexagonal phase and the (2 1 1) aluminium texture. The diffuse diffraction lines with hexagonal symmetry obsserved in this pattern are due to the very thin layered character of the hexagonal phase.

In order to differentiate the hexagonal phase from the aluminium matrix, some dark-field images were analysed. We have selected a typical orthogonal diagram with extra aluminium texture diffraction spots (Fig. 5b) which corresponds to the area included in Fig. 5a. The dark-field image due to the (1 1 0) reflection of the hexagonal phase is shown in Fig. 5c and the image due to the (1 1 1) reflection of aluminium is included in Fig. 5d. From these micrographs it can be seen that in the central part of the eutectic metastable structure, the hexagonal phase grows as a wide semicircular and concentric laminar structure and the aluminium crystals appear at the interlaminar sites. In the outer part, the radial structure is an alternating structure formed by aluminium and the hexagonal phase with some faceted voids overlapped.

It is important to note that the metastable laminar structure is very sensitive to the electron-beam intensity. When the beam intensity was high, we could observe *in situ* in the TEM the precipitation of germanium and aluminium.

Finally, let us refer to the laser exposure-time dependence on the observed microstructure. Its general behaviour and the morphology for 50 and 5 μsec exposures are very similar. Nevertheless, a very important result has been obtained, since no metastable hexagonal phase could be detected in the melted area at 5 μsec exposures. This result supports the previous conclusion [3] that the metastable hexagonal phase is not formed at high cooling rates.

4. Conclusions

When irradiating thin films of $Al_{59}Ge_{41}$ with 50 μsec laser pulses and an irradiation power in the 8 to 28 mW range, we have obtained a laminar eutectic metastable structure. When the cooling rate is increased by irradiating with 5 μsec pulses, the metastable structure was not found. This structure is composed of by alternating layers of aluminium and a germanium-rich metastable hexagonal phase.

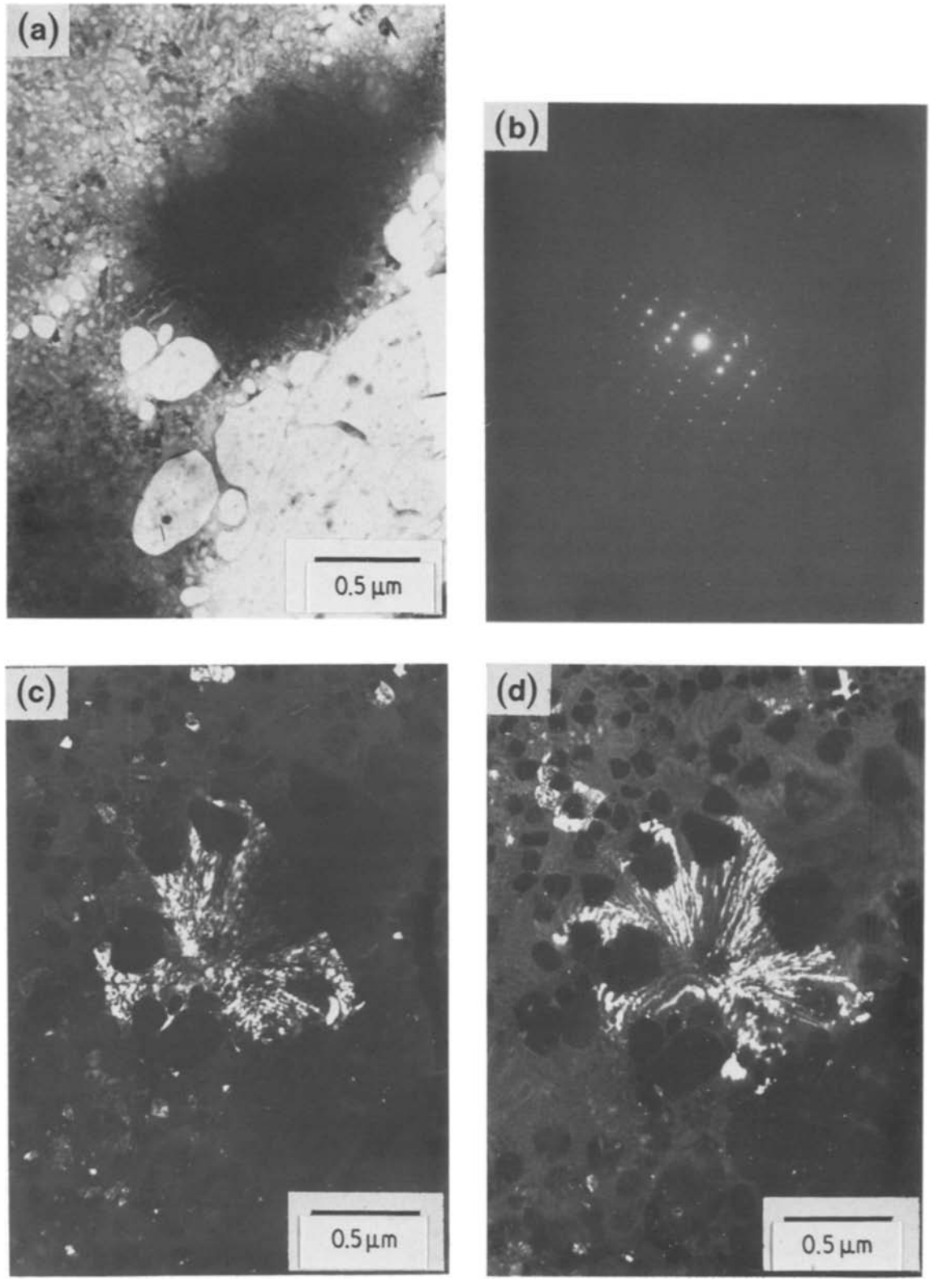

Figure 5 Bright-field image of the metastable structure (a) and its typical orthogonal SADP (b). The dark-field images were obtained using the (1 1 0) metastable phase reflection (c) and the (1 1 1) aluminium texture reflection (d).

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