



## Kinetics and crystal texture improvements on thin germanium layers obtained by aluminium induced crystallization using oxygen plasma

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### ABSTRACT

The fabrication of strongly-textured thin crystalline germanium layers on amorphous silica substrates can be achieved by aluminium induced crystallization using the 'aluminium induced layer exchange' mechanism. This requires a diffusion barrier, or interlayer, between the Al and Ge layers with a specific chemistry. We investigate here the effect of oxygen plasma on this interlayer as an alternative route to the standard air-exposure process. We find that the plasma treatment strongly slows down the kinetics of the crystallization. This can be compensated by a higher process temperature, after which the defect density becomes similar to that of air-oxidized but with defects of smaller size. This substantially improves the overall texture of the Ge layer and a near complete (111) orientation is obtained.

### 1. Introduction

Germanium recrystallization on foreign substrates such as plastic or glass has received particular attention due to the interesting properties of crystalline Ge for low cost photovoltaics [1–3] or relatively inexpensive transistor applications [4,5], in which high absorption coefficient or specific semiconductor properties are desirable. Metal induced crystallization is a proven technique that allows one to substantially decrease the crystallization temperature of amorphous Ge. Standard solid phase crystallization occurs around 500–600 °C for Ge [6] and various metals can be used to facilitate crystallization [6]. Aluminium and gold are promising candidates with the lowest temperatures reported for the metal induced crystallization (eutectic temperature are respectively 420 °C and 360 °C) [7]. Aluminium Induced Crystallization (AIC) may be the most interesting technique for low-cost large-surface application because of the reduced cost of aluminium compared to gold.

Investigation of the AIC of amorphous Ge has shown that crystallization follows a particular sequence during which the Al and Ge layers inverse their positions [8–10]. This specific mechanism, referred to as Aluminium Induced Layer Exchange (ALILE), was first observed by Nast et al. [11] in the case of Si. The ALILE process can be improved by adding a diffusion barrier or 'interlayer' between the Al and Ge layers. The importance of this 'interlayer' was first demonstrated for the AIC of

Si, with the fabrication of (111)-oriented layers with large grains by Kurosawa et al. [12] but it also applies to the AIC of Ge [8–10]. In 'reverse' AIC samples, the Al layer is initially above the amorphous Ge. In this case, the most common interlayer (diffusion barrier) is GeO<sub>x</sub>, directly obtained by the oxidation of the bottom Ge layer, before the top Al layer is deposited. Air-oxidation can also be used [13] as well as ozone exposure [9,14]. In 'direct' AIC samples, the Al layer is initially below the amorphous Ge. In this case, the most common material used as interlayer is AlO<sub>x</sub>. Air-oxidation of the Al layer has been used and optimized in several studies [8,10,15,16].

In both the 'reverse' and 'direct' Ge-AIC, the chemistry of the interlayer has a strong impact on the kinetics of crystallization. Recently, silver-based compounds have been investigated for the AIC of Ge with a focus on the interlayer chemistry [17]. More conventional solutions make use of AlGeO<sub>x</sub> interlayers obtained by evaporating a thin Ge layer (~1 nm) on top of the Al layer [18,19]. The subsequent air oxidation is believed to produce an interlayer composed of AlO<sub>x</sub> or GeO<sub>x</sub> compounds, which decreases the annealing temperature required for the ALILE process. This is currently understood as due to the Ge atoms diffusing more quickly in GeO<sub>x</sub> than AlO<sub>x</sub>, therefore promoting a faster nucleation and lateral growth of the Ge crystals.

In the present work, we investigate the use of an oxygen plasma treatment compared to the standard air oxidation to vary the chemistry of the interlayer. We study the effect of strong or partial

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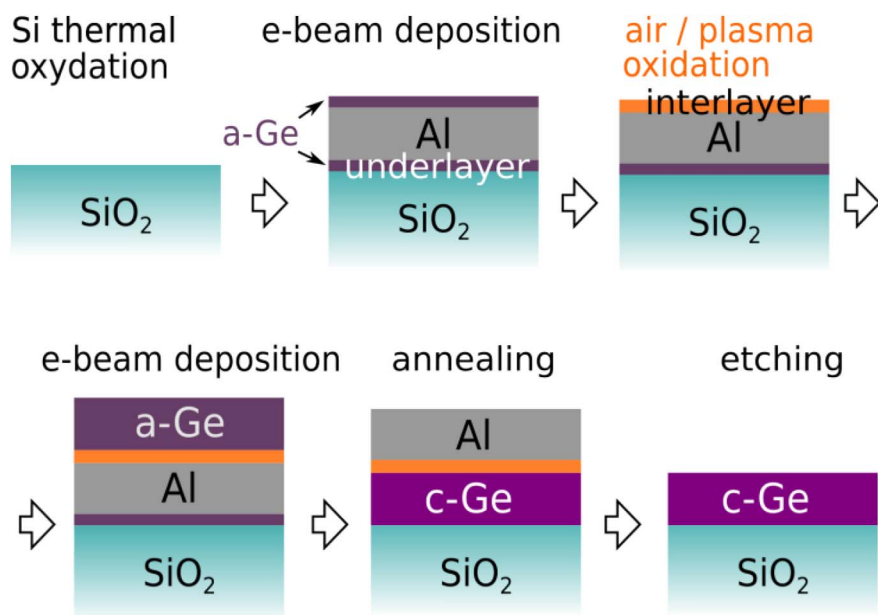


Fig. 1. Schematics of Al-Ge bilayer deposition sequence on thermal silica using a-Ge underlayer and an AlGe interlayer. The amorphous Ge (a-Ge) crystallizes during annealing (producing c-Ge) and exchanges position with the Al layer. The Al layer is then chemically removed to obtain a crystalline Ge layer on silica.

oxidation of the  $\text{AlGeO}_x$  interlayer, without changing the other deposition parameters.

## 2. Material and methods

We use electron beam evaporation (Plassys MEB 550SL) to deposit the layered structure shown in Fig. 1. The host substrate is a thermally oxidized Si (100) 2" or 4" wafer with a typical 30–40 nm thickness of silica (1050 °C for 15 min). We first deposit 1 nm of Ge as a wetting layer or ‘underlayer’ (rate 0.01 nm/s) aimed at speeding up the AIC process [20] and obtaining a smoother surface [21]. The main 20 nm thick Al layer is deposited at a rate of 2 nm/s. Another thin Ge layer  $\sim 1.5$  nm (0.1 nm/s) is deposited on the top of the Al, so that the subsequent surface oxidation yields a mixed  $\text{AlGeO}_x$  interlayer instead of pure  $\text{AlO}_x$ . The oxidation of this ‘interlayer’ can be performed simply in air (between 9 and 118 min) or alternatively by oxygen plasma (RF power: 5 W, flux of 10 sccm  $\text{O}_2$  at 50 mTorr, during 0.5–2 min). Finally, the main 20 nm Ge layer is deposited at a rate of 1 nm/s using the same e-beam evaporator.

The samples are then annealed in a closed programmable hotplate (HARRY GESTIGKEIT) under nitrogen flow. An in situ microscope [22] allows us a direct optical characterization of the sample during the annealing. Two long working distance objectives are used to provide high resolution ( $50\times$ ) or large field images ( $20\times$ ).

Wet etching by,  $\text{H}_3\text{PO}_4$  (for 20 s at 60 °C), is used to remove the top Al layer after the layer inversion of the ALILE process so that only the crystallized Ge islands remain on the silica surface.

Chemical analysis is performed using Energy Dispersive X-ray Spectroscopy (EDXS) in a Scanning Electron Microscope (SEM FEI Magellan fitted with Oxford INCA EDXS detector).

Grazing Incidence X-ray Diffraction (GIXRD) is performed in a Rigaku SmartLab equipped with a Cu rotating anode to characterize the Ge layer crystallinity (using the Cu K $\alpha$  line).

Electron backscatter diffraction (EBSD) is also performed to confirm the crystallographic orientation in a SEM (ZEISS Supra 55 VP, Hikari/OIM TSL EDAX).

## 3. Results

Fig. 2(a) and (b) present standard ex-situ characterizations by optical microscopy of the two samples respectively obtained by air and plasma oxidation. In both cases, we obtain irregular crystalline Ge islands (light blue or light green) on the  $\text{SiO}_2$  surface (dark blue) after the removal of the top Al layer by wet-etching (see Fig. 1). The sample with an ‘interlayer’ (diffusion barrier) obtained by plasma treatment, Fig. 2(b), has a smaller surface coverage, about 76%, than that obtained using air oxidation (Fig. 2(a), about  $\sim 80\%$ ). Both samples have defective areas (indicated by arrows) that we have investigated in a previous study [22]. Configuration for GIXRD characterization is shown in Fig. 2(c). The incident angle for X-ray beam is  $\omega = 0.3^\circ$  with respect to the sample surface. In this configuration, the X-ray source and the sample are fixed, while the detector is rotating in the plane of the sample along the angle  $2\theta\chi$ . The GIXRD analysis, Fig. 2(d), compares the diffracted intensities for the plasma-treated and air-oxidized samples. Reference data for powder Ge (ICDD card 00-004-0545) is provided for comparison with a fully randomly-oriented sample. The geometry of GIXRD is such that Bragg conditions are only satisfied by planes perpendicular to the surface of the sample, see Fig. 2(c). Therefore, a pure  $\langle 111 \rangle$  texture (along the vertical direction) is not characterized by a 111 diffracted intensity but by the presence of the 220, 422 and 440 diffracted beams, which all lie in directions perpendicular to  $\langle 111 \rangle$ . We conclude from the analysis of the GIXRD diffractogram Fig. 2(d) that the plasma treated sample has a near complete  $\langle 111 \rangle$  texture. The air-oxidized sample only shows a partial  $\langle 111 \rangle$  texture, as an intermediate situation between a fully random orientation and a complete  $\langle 111 \rangle$  texture.

To confirm the crystallographic orientation obtained by GIXRD (Fig. 2), we perform EBSD characterization. The normal of the Ge crystallites projected along the vertical direction is shown in Fig. 3(a) for the sample with the air-oxidized ‘interlayer’ and in Fig. 3(c) for the plasma-treated sample. The corresponding in-plane orientations are respectively shown Fig. 3(b) and (d). Both samples show a high  $\langle 111 \rangle$  texture, blue color in Fig. 3(a) and (c), but the air-oxidized

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