# Improvement on MIS Properties of Single-Grain Germanium by Pulsed-Laser Annealing

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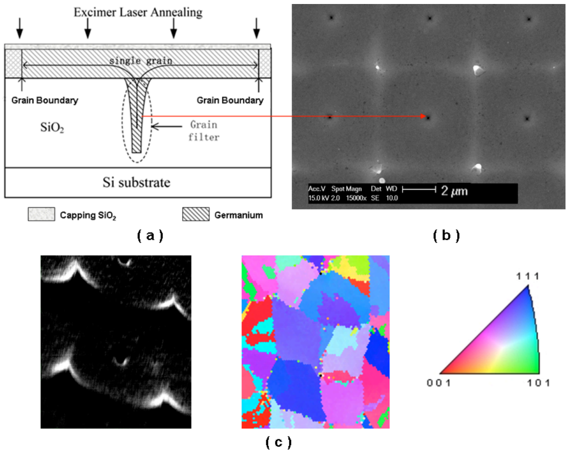
Germanium (Ge) has been receiving wide attention because of its significantly high mobility and narrow band-gap compared with silicon.[1] It is a very promising material candidate in ULSI, TFT and image sensor fields. However, there is still a critical challenge to obtain Ge MIS structure with good interface properties. Many attempts have been made with different passivation methods[2,3] and it has been reported comparatively low interface trap density ($<10^{11}\mathrm{eV}^{-1}\mathrm{cm}^{-2}$) with stacked high-k material. However, most of the current techniques are based on thermal or plasma oxidation on bulk Ge or Germanium on Insulator (GOI) wafer and very few based on thin-film Ge has been published. The main reason is that Ge-O bonds inevitably exist at the Ge/oxide interface during low thermal-budget thin-film process and GeO desorption would cause serious deterioration at the surface of Ge layer. In this paper, we propose pulsed-laser annealing before crystallization of Ge thin film to obtain chemically stable and electrically excellent MIS properties. We investigated effects of pre-annealing by pulsed laser before crystallization on MIS properties of the Ge thin film.

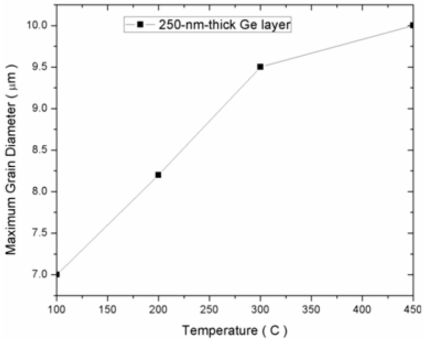


(a) (b) (c)

Fig.1 (a) Structure of Germanium μ-Czochralski Process; (b) SEM of the Germanium grains after crystallization; (c) EBSD mapping images.

As depicted in Fig. 1(a), the μ-Czochralski process based on excimer-laser crystallization was used for 2D location control of Ge grains.[4] 50nm PECVD TEOS SiO$_2$ was deposited on top of sputtered a-Ge film as capping layer. Upon low-energy excimer-laser pre-annealing, the Ge surface absorbs the light and heats up. Followed by high-energy excimer-laser crystallization irradiation, the Ge would eventually melt completely, but the grain-filter won't be melted. The surface GeO is also completely melted. Due to the presence of capping SiO$_2$, it would not desorb but be kept at the interface. After turning off the laser pulse, the molten Ge starts solidifying and only single grain can be filtered out by the grain filter with gentle–slope sidewall. At the end of the solidification of Ge, it is expected that a thin, high-quality layer dominated by GeO$_2$ is grown at the interface between crystalline single-grain Ge and SiO$_2$, which means the bonding condition has reached equilibrium dominated by Ge-O$_2$ (4+ state).

SEM of Ge grains after crystallization (Fig. 1(b)) shows grains with array pitch of 6μm are obtained on the predetermined positions of the grain-filters. The electron backscattering diffraction (EBSD) (Fig. 1 (c)) shows the surface crystallographic orientations. At higher substrate temperature during laser crystallization, we can get larger grain size, which is shown in Fig. 2 (a). With increasing the Ge film thickness to 500nm, the maximum diameter can reach 9.5μm as summarized in Fig. 2(b). Figure 3 shows that tens of nanometer-scale voids are observed in SEM images, which we suspect is due to GeO formed at the interface between Ge and GeO$_2$ and GeO desorption causes higher pressure locally.[5] The



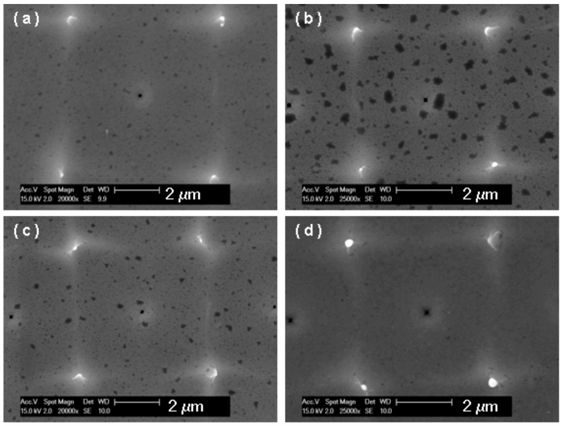
(a)

| Thickness ( nm ) | Process Window ( mJ/cm$^2$ ) | Max. Grain Size ( μm ) |
|---|---|---|
| 250 | 350 - 450 | 10.2 |
| 500 | 500 - 640 | 9.5 |

(b)

Fig.2 (a) Maximum grain size as function of substrate temperature; (b) Summary of different-thickness germanium crystallization.

size of the voids increases with time as shown in Fig. 3. The pre-annealing energy and number of pulses were optimized to release the gas pressure of oxygen induced during the previous process and decrease the chance of GeO desorption. In Fig.3, it is proved by comparing surface deterioration of the 4 samples that multiple-pulse pre-annealing with high energy is effective to suppress the GeO desorption and helpful to form high-quality passivation layer. More detail about the interface is analyzed in Fig. 4 showing Bright-Field Transmission Electron Microscopy (BFTEM) cross-section image of sample prepared by in-situ FIB lift-out technique and locally capped with Pt prior to the imaging. Energy Dispersive Spectroscopy (EDS) analysis was applied at the interface and composition of Ge to O is normalized to around 1:2 (Ge : Si : O = 29.3% : 5.6% : 65.1%), which indicates the $GeO_2$ formed at the interface. Further XPS analysis to characterize atomic bonding energy is undergoing.



| Item | Sample ( a ) | Sample ( b ) | Sample ( c ) | Sample ( d ) |
|---|---|---|---|---|
| Pre-Annealing | 100 mJ/cm$^2$ x 1 | 100 mJ/cm$^2$ x 1 | 275 mJ/cm$^2$ x 1 | 100 mJ/cm$^2$ x 80 |
| Crystallization | 420 mJ/cm$^2$ | 425 mJ/cm$^2$ | 425 mJ/cm$^2$ | 420 mJ/cm$^2$ |
| Storage Time | 1 hour | 1 year | 1 year | 1 hour |

Fig.3 SEM of surface deterioration of Ge grains under different crystallization conditions.

After 1.4 µm-thick aluminium sputtered and patterned on top of capping oxide, C-V measurement is performed by special top-to-top structure since there is no conductive substrate. Very small frequency dispersion from 50kHz to 10MHz is observed in Fig. 5. Minimum $D_{it}$ value is estimated to be 3.4E11 $eV^{-1}cm^{-2}$ extracted by the capacitance-voltage method. The bi-direction C-V characteristics in Fig. 6 show very little hysteresis indicating the low trap state density and small amount of mobile charges at the interface.

In summary, by optimizing pulsed-laser pre-annealing and crystallization conditions, we can achieve a high-quality crystallized thin-film Ge MIS structure. Through the use of the capping oxide layer prior to the laser crystallization, the interface with low trap density between oxide layer and germanium could be formed and GeO deterioration could be suppressed a lot. Based on this thin-film crystallized germanium MIS structure, future applications include large-area high-speed display panel, wide-absorption-spectrum image sensor, optical inter-connection, flexible and three-dimensional CMOS integration.

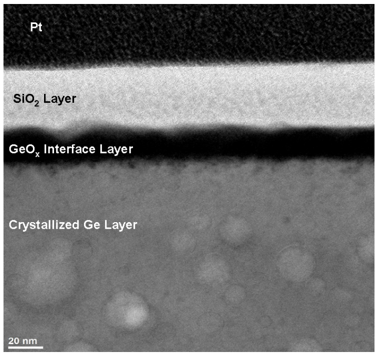


Fig.4 Cross-section FBTEM image of crystallized Ge capped with silicon-dioxide layer.

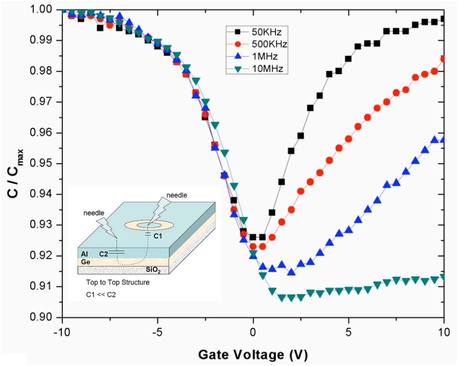


Fig.5 Normalized C-V characteristics of Al/$SiO_2$/GeOx/Ge MIS structure.

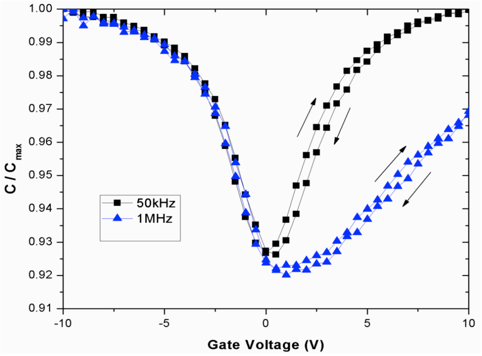


Fig.6 Bi-directional C-V characteristics of Al/$SiO_2$/$GeO_x$/Ge MIS structure under high and low frequencies.

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