Study of amorphous Cu-Te-Si thin films showing high thermal stability for application as a cation supply layer in conductive bridge random access memory devices

Wouter Devulder^{*,a,b}, Karl Opsomer^b, Matthias M. Minjauw^a, Johan Meersschaut^b, Malgorzata Jurczak^b, Ludovic Goux^b and Christophe Detavernier^a

^aGhent University, Dept. of Solid State Sciences, Krijgslaan 281 (S1), 9000 Ghent, Belgium ^bIMEC, Kapeldreef 75, 3001 Leuven, Belgium

Email: <u>Wouter.Devulder@UGent.be</u> <u>Wouter.Devulder@imec.be</u>

Phone: +32 (0) 9 264 43 48 Fax: +32 (0) 9 264 49 96

1. Kissinger analysis

The activation energy for crystallization of a CuTeC20, CuTeGe20 and CuTeSi20 layer is determined by the Kissinger method [1]. The method requires the knowledge of the temperature at which an equivalent stage of reaction occurs for different heating rates. The method assumes a maximum reaction rate at the peak temperature T_p of crystallization. This also implies a constant degree of conversion at this stage [1]. In this work, in situ XRD is used to determine the crystallization temperature T_x of the alloy, which is used as T_p . The 50 nm CuTeC20 and CuTeGe20 layers were deposited by means of magnetron sputter deposition on 20 nm Al₂O₃/Si substrates, as described elsewhere [2, 3]. The composition of the CuTeC20 layer was verified by means of EDX (as described in [2]) and the composition of the CuTeGe20 layer by XRF (as described in [3]). The compositions are summarized in Table S1. The samples were then annealed at different heating rates ranging from 0.1°C/s to 5°C/s in He atmosphere and the XRD spectrum was recorded. The crystallization temperature T_x is then defined as the temperature in the temperature interval [T_{start}, T_{end}] where the maximum intensity change occurs in the selected 2 Θ range [Θ_{min} , Θ_{max}], as is illustrated in Figure S1. This 2Θ range is selected based on the diffraction peaks of the phase that first crystallizes. This is illustrated in Figure S1 for the three different materials, annealed at a heating rate of 0.5° C/s. Using the relation [1]

$$\ln\left[\left(\frac{dT}{dt}\right)\frac{1}{T_x^2}\right] = -\frac{E_A}{k_B T_x} + C,$$

the activation energy E_A can be extracted. In this equation (dT/dt) is the heating rate, T_x the crystallization temperature, k_B the Boltzmann constant and C is a constant. By plotting $ln((dT/dt)/T_x^2)$ as a function of $1/k_BT_x$, E_A is extracted from a linear fit, as illustrated in Figure 4 in the manuscript.

Material	Cu (at%)	Te (at%)	Alloying element (at%)
CuTeSi20	50.7	31.8	17.5 (Si)
CuTeC20	49.4	32.8	17.8 (C)
CuTeGe20	48	30.5	21.5 (Ge)

Table S1: Compositions of the layers used for Kissinger analysis.



Figure S1: In situ XRD patterns of a (a) CuTeC20, (b) CuTeGe20 and (c) CuTeSi20 layer, collected at a heating rate of 0.5° C/s in He. The graphs at the right show the integrated intensity in the $[\Theta_{min}, \Theta_{max}]$ region as a function of the temperature. The crystallization temperature T_x is determined as the temperature where the maximum increase in integrated intensity occurs in the temperature range $[T_{start}, T_{end}]$.

2. References

[1] Advances in Crystallization Processes, Edited by Y. Mastai, 2012

[2] Devulder, W.; Opsomer, K.; Seidel, F.; Belmonte, A.; Muller, R.; De Schutter, B.; Bender, H.; Vandervorst, W.; Van Elshocht, S.; Jurczak, M.; Goux, L. & Detavernier, C., ACS Appl. Mater. Interfaces, 2013, 5, 6984-6989

[3] Devulder, W.; Opsomer, K.; Rampelberg, G.; De Schutter, B.; Devloo-Casier, K.; Jurczak, M.; Goux, L. & Detavernier, C., *J. Mater. Chem. C*, **2015**, *3*, 12469-12476