Non-stoichiometry in Phase Change Memory Materials

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Phase change memory materials (PCMM) are formed by a large group of chalcogenides, mostly tellurides and selenides, but can be formed also by Sb-rich alloys of Ge, Ga, Ag, In, by other elements and by some inter-metallic or intermediate compounds. Their application in optical and electrical memories is based on different electrical conductivity or optical reflectivity of their glassy and crystalline phases.

The phase transition between glassy (amorphous) state to the crystalline one shall be fast, which limits the choice of proper materials. From our results and from the large amount of published materials (see, e.g. (Yamada, Ohno et al. 1991; Yamada and Matsunaga 2000; Yamada, Kojima et al. 2002; Kolobov 2003; Frumar 2007; Raoux and Wuttig 2009)) it is clear that the composition of PCMM described and of those already applied does not often correspond to a stoichiometric compound. Composition of many PCMM can be changed in broad regions not only in amorphous (glassy) state, which is common feature of glasses, but also in crystalline state that is relatively rare. The changes of stoichiometry can be several orders larger than in classical semiconducting crystals in spite of the fact that many crystalline phases of PCMM and of their amorphous (glassy) states are semiconductors too. The reasons for such behavior are chemical similarities of many elements forming PCMM, their similar physical properties, similar energy of bonds and thermodynamic factors.

The problems and consequences of non-stoichiometry in many PCMM, the thermodynamic and kinetic aspects of formation of metastable and stable solid solutions based on PCMM compounds are discussed. Discussed is not only glassy state of PCMM, its properties and composition, but also the metastable cubic structure of many PCMM crystals and the hexagonal, equilibrium modification of some Ge-Sb-Te and Sb-rich PCMM (e.g. Sb_2Te_3, Sb_2Se_3, $GeSb_2Te_4$, $Ge_2Sb_2Te_5$, $GeSb_4Te_7$, Sb-Te, Sb-Ge, Ag-In- Sb-Te, etc.).

The kinetic reasons for formation of metastable crystals by fast crystallization are also discussed.

The knowledge of physicochemical properties of PCMM, understanding of their structure and behavior can help to choice of materials with better parameters for the next generations of electrical optical memories.

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REFERENCES

1. Yamada N. et al.: J. Appl. Phys. 69, (1991) 2849
2. Yamada N., Matsunaga T. : J. Appl. Phys. 88, (2000) 7020
3. Yamada N. et al.: proc SPIE 4342 (2001)55
4. Kolobov A.V. (Ed), Photoinduced Metastability of Amorphous Semiconductors, Willey- VCH, Weinheim 2003.
5. Raoux S. Wuttig M. (Eds.), Phase Change Materials, Science and Application, Springer, New York 2009.
6. Frumar M. et al., "Phase Change Memory Materials-Composition, Structure and Properties." J. Mat. Sci.: Mater. Electron **18**: 169-174J. Mat. Sci.: Mater. Electron. 18, (2007)169.

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