Structural Transformations in Amorphous ↔ Crystalline Phase Change of GaSb

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Introduction

The development of nonvolatile memories with ultrafast read/write speed, based on amorphous ↔ crystalline transformation in phase-change materials (PCMs) is of enormous technological interest [1]. Recently it was shown that Ga-Sb alloys can provide enhanced performance as PCMs [2]. However, the atomic scale mechanism of the amorphous ↔ crystalline phase change process in this system is poorly understood [3]. Here we present the results of high-field multinuclear (^{71}Ga and ^{121}Sb) NMR spectroscopic study of GaSb, in their amorphous and thermally crystallized states, to directly address the nature of structural changes associated with the phase change process.

Experimental

Amorphous films of GaSb (50 at.% Ga) with 300 nm thickness were deposited using DC magnetron sputtering and were lifted off for subsequent NMR measurements. The ^{71}Ga MAS NMR spectra of the as-deposited amorphous film and its crystallized product were collected at the NHMFL with a Bruker DRX spectrometer at 19.6 T and 25 kHz MAS. The ^{121}Sb NMR spectra were collected using the same system and the WURST/QCPMG pulse sequence.

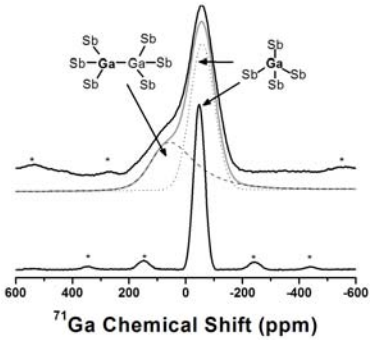

Fig. 1. ^{71}Ga MAS NMR spectra of crystalline GaSb (bottom) and amorphous GaSb film (top).

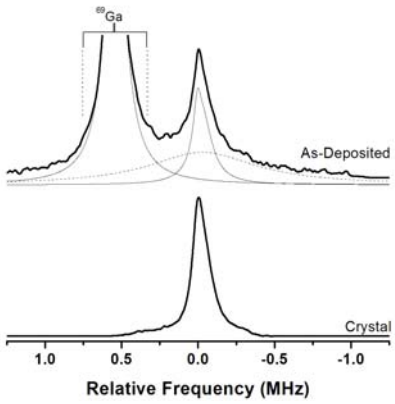

Fig. 2. ^{121}Sb WURST/QCPMG NMR spectra of amorphous (top) and crystalline GaSb (bottom).

Results and Discussion

The ^{71}Ga MAS NMR spectrum of amorphous GaSb (*a*-GaSb) film is compared in Fig. 1 with that of the GaSb crystal. The crystal is characterized by a relatively narrow resonance centered at –50 ppm that corresponds to the Ga atoms in tetrahedral coordination with Sb. The spectrum of *a*-GaSb, on the other hand, is characterized by two resonances; the dominant signal at –60 ppm is assigned to $GaSb_4$ tetrahedral environments as in the bulk crystal. The partially resolved shoulder observed near 100 ppm, broadened by quadrupolar interaction (Fig. 1) is consistent with the presence of Ga-Ga homopolar bonds, presumably corresponding to tetrahedra with one Ga-Ga and three Ga-Sb bonds forming ethane-like Ga_2Sb_6 environments (see Fig. 1) in the amorphous phase. The presence of Ga-Ga bonding implies the formation of an equivalent amount of Sb-Sb bonds in Sb**Sb**Ga_3 tetrahedra in *a*-GaSb. The ^{121}Sb WURST/QCPMG NMR spectra of amorphous and crystalline GaSb are compared in Fig. 2. The spectrum of the GaSb crystal shows a relatively narrow (FWHM ~ 0.12 MHz) peak consistent with the cubic symmetry of $SbGa_4$ tetrahedral environments. The ^{121}Sb line-shape of *a*-GaSb clearly shows this narrow component corresponding to the $SbGa_4$ environment, superimposed on a broad component with large quadrupolar coupling constant that can indeed be associated with the formation of Sb-Sb bonds (Fig. 2).

Conclusions

The Ga and Sb atoms are fourfold coordinated in *a*-GaSb with nearly 40% of these atoms being involved in Ga-Ga and Sb-Sb bonding. Crystallization of *a*-GaSb involves elimination of these homopolar bonds via bond switching and significant structural reconstruction that must play an important role in the phase change kinetics of GaSb for PCM applications.

Acknowledgements

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References

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