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In-situ TEM Observation of Ni_xAs_y Nanosheet Formation by Inter-diffusion of Ni into Black As

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2D layered materials have attracted a lot of attention in recent years owing to its intriguing properties which are beneficial for nanoelectronic and photonic applications [1, 2]. These materials have shown to exhibit versatile electronic properties, including semiconducting, metallic, superconducting, and topological insulator properties with high mobility. Layered materials like graphene, silicine, black phosphorous, boron-nitride nanosheets, and transition metal dichalcogenides (TMDs) have been theoretically speculated and experimentally established to possess exotic properties [2-4]. Such discoveries have opened a new frontier in nanotechnology research. Therefore, in recent times, a lot of effort is being focused on discovering newer materials with similar properties. In that regard, black arsenic (b-As), a rare allotrope of As, has shown remarkable in-plane anisotropy which makes b-As, and its analogues, promising materials in this research area [4, 5].

In this study, we show a novel yet simple route to synthesize Ni_xAs_y nanosheet by inter-diffusion of nickel (Ni) into black arsenic (b-As) template. In-situ TEM observation of the reaction, give insights into the formation mechanism. TEM/STEM imaging was performed using a FEI F30 and aberration-corrected Titan G2 60-300 kV fitted with Super-X system for EDS analysis. The cross-sectional Ni/As TEM sample on Cu half-grid, was prepared using dual beam FEI FIB. The heating experiment was carried out using a Gatan heating holder. Figure 1a-f shows the BF-TEM image of the lamella as it is heated to different temperature and/or time. The Ni gradually diffuses into the b-As layer at ~298°C.

Figure 2a shows the BF-TEM image of a typical transformed region at higher magnification, revealing that the Ni has migrated to the b-As layer. High resolution TEM image (Figure 2b) shows fringes corresponding to the (101) plane of $NiAs_2$. To gain further insights into the formation of the new phase, additional investigations were carried out in STEM mode. Figure 2c, d shows ADF STEM images before and after the heating experiment. EDS analysis of the sample, before heating, revealed that the Ni layer is distinctly separate from the As layer, with about 15 nm of overlap layer. However, analysis after the heating experiment shows a homogeneous molar composition of Ni and As in the bottom layer indicating uniform mixing of the diffused Ni in the b-As layer. An average composition of ~24% Ni and 76% As was observed throughout the layer [6].

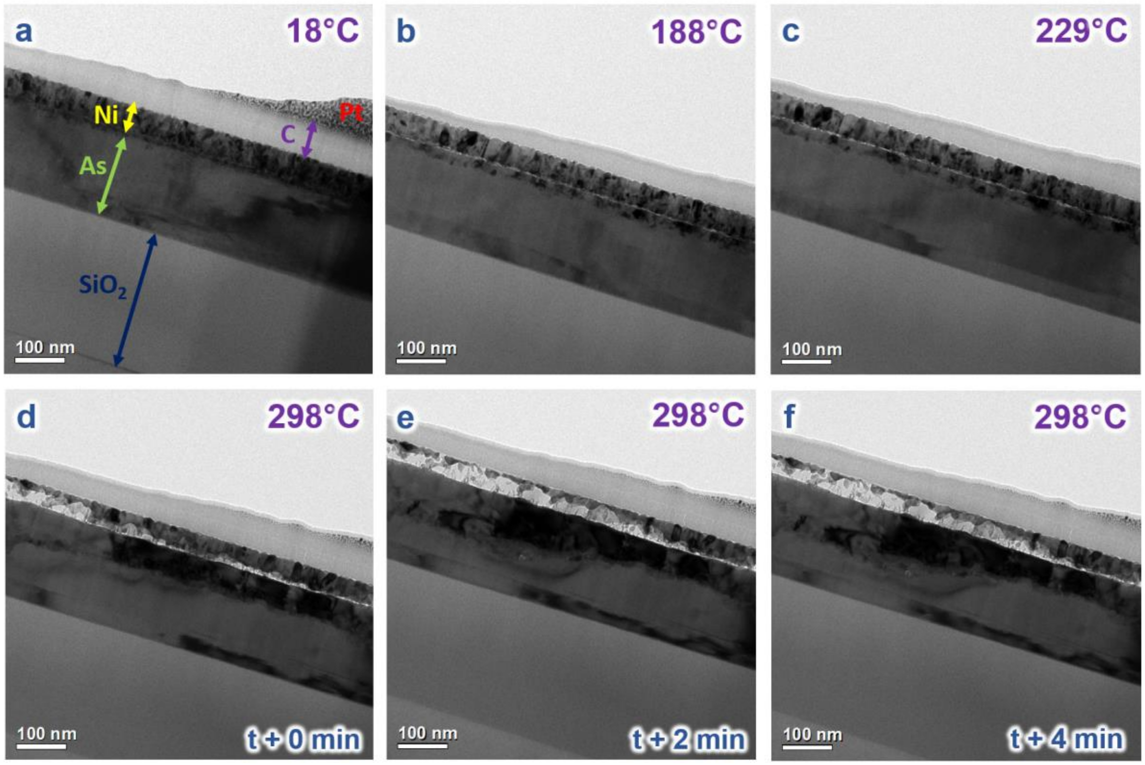

Figure 1. (a-f) BF-TEM image of the FIB sectioned Ni/b-As lamella at different temperature and/or time. The individual layers are marked in image-(a). Ni starts to diffuse into the b-As layer at ~298°C.

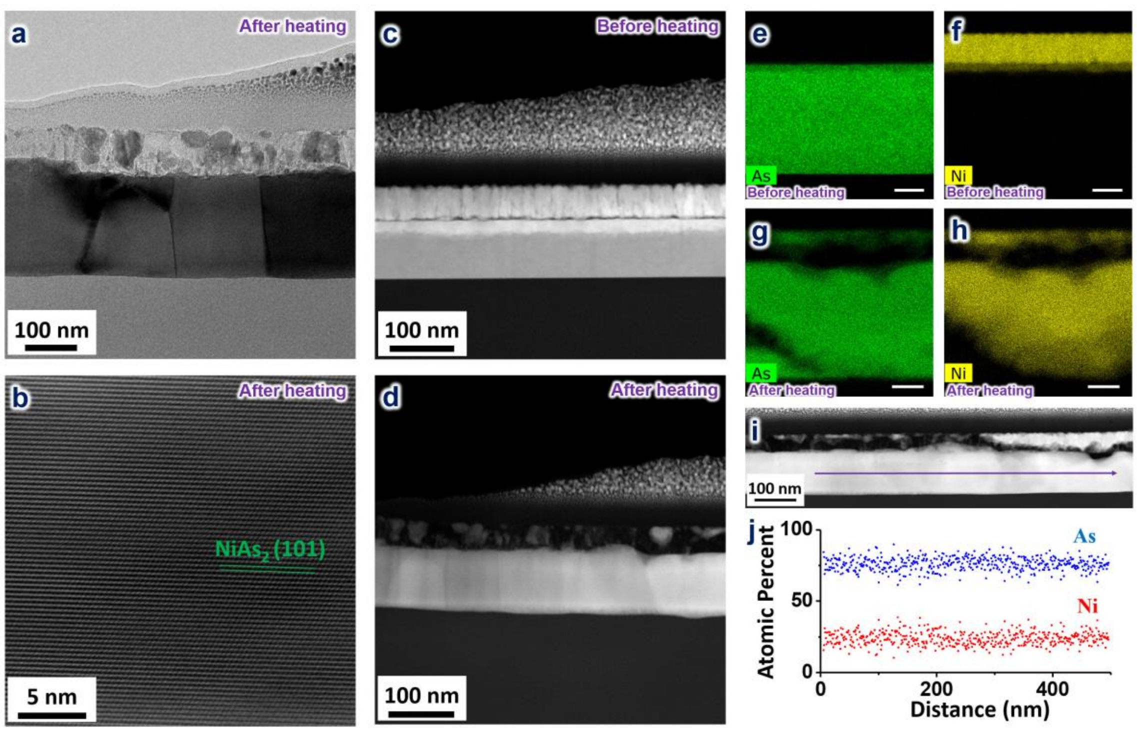

Figure 2. (a) BF-TEM image showing the Ni diffused b-As layer, after the heating experiment. (b) HR-TEM image shows fringes corresponding to (101) plane of NiAs2. (c & d) ADF-STEM image of the Ni and b-As layer before and after the heating experiment, respectively. (e-h) EDS maps of As-K (green) and

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Ni-K (yellow) before and after the heating experiments (Scale bar- 50 nm). (i & j) EDS line scan is obtained along the NiAs2 layer, as marked by the purple arrow. The quantified molar percentage of Ni (red) and As (blue) is plotted as a function of distance along the indicated purple arrow.

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