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Bridgman Growth of NiSb Single Crystals

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Abstract—Structurally perfect NiSb single crystals ≃25 mm in diameter and 250 mm in length were grown by the Bridgman method. Polishing etch compositions were selected for the preparation of NiSb substrate surfaces.

Nickel antimonide belongs to the family of pnictides—intermetallic compounds of 3*d* transition metals with Group V elements. In nature, nickel antimonide occurs as the mineral breithauptite. In recent years, pnictides have been used in heterostructures composed of a ferromagnetic intermetallic compound and semiconductor, which have considerable potential for application in spintronics [1–3].

According to earlier results [4], nickel antimonide melts congruently at 1153°C and has a rather broad homogeneity range: it dissolves 3 at % Sb and ≃4 at % Ni.

Czochralski-grown NiSb single crystals [5] had a rather low structural perfection and consisted of mosaic blocks. It was of interest to develop a process for the growth of large, high-quality NiSb single crystals suitable for the fabrication of substrates.

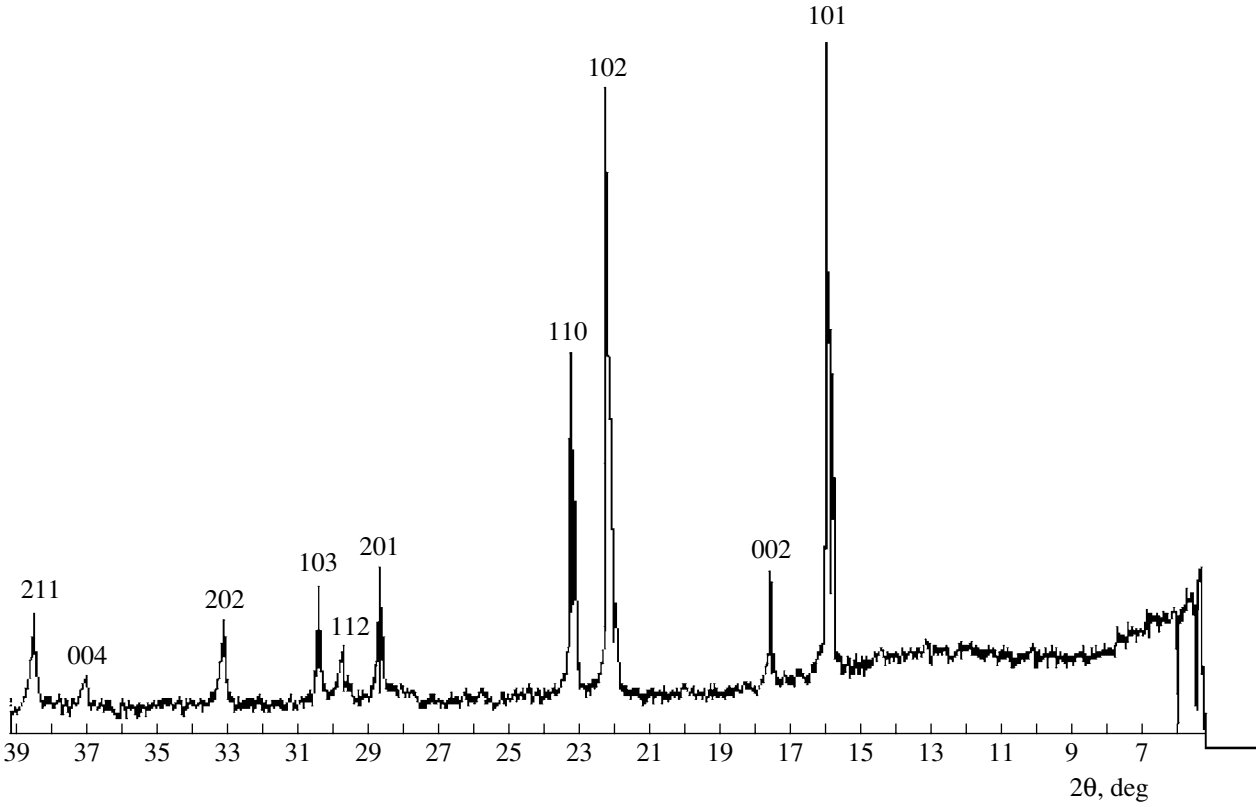

Fig. 1. XRD pattern of NiSb.

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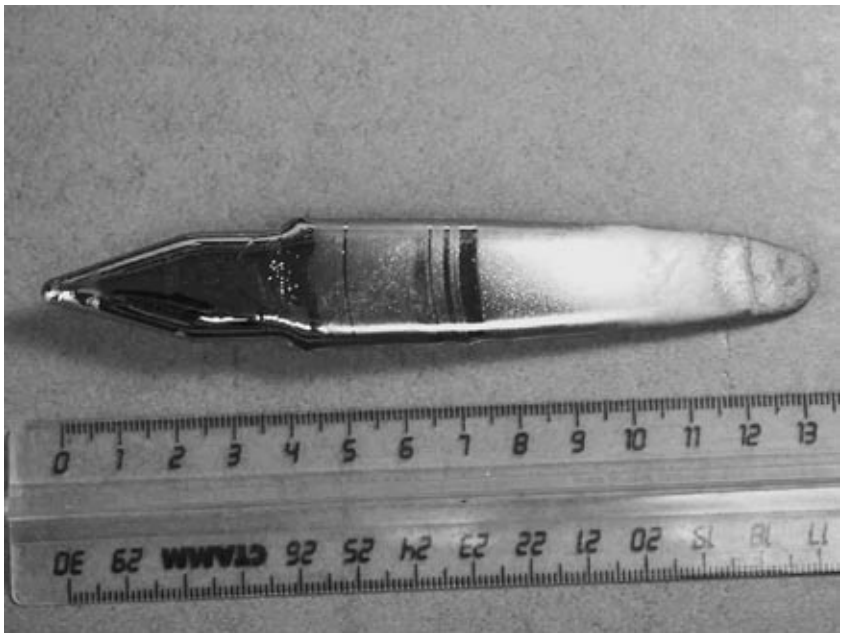

Fig. 2. Bridgman-grown NiSb crystal.

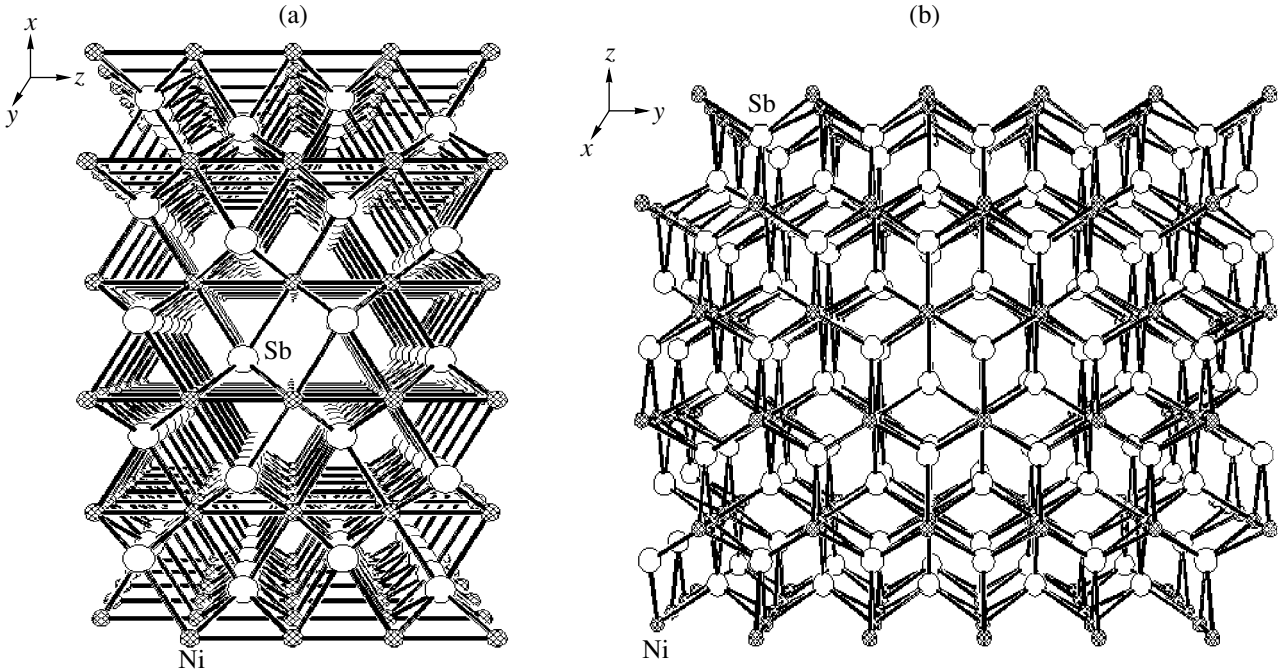

Fig. 3. Crystal structure of NiSb projected along the (a) [010] and (b) [100] directions.

The growth charge was prepared from a stoichiometric mixture of electrolytic nickel and V-5 antimony, which were sealed in a silica ampule under a vacuum of 10^{-2} Pa. The ampule was then mounted in a vertical furnace fitted with a massive steel block for producing a uniform temperature profile along the length of the ampule. After heating to 640°C, the temperature was maintained constant for 3 h, which led to the melting of antimony and partial reaction between Sb and Ni. Next, the temperature was raised to the melting point of NiSb (1153°C) at a rate of 30°C/h and then maintained constant for at least 6 h, followed by furnace-cooling. The temperature was monitored with a Pt/Pt–Rh thermocouple and controlled by a RIF-101 unit.

The resultant samples, pale rose in appearance, were characterized by x-ray diffraction (XRD) and differential thermal analysis (DTA).

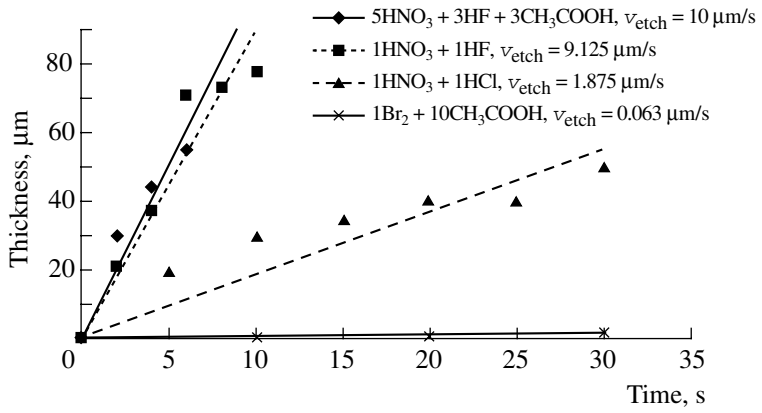

Fig. 4. Thickness of the layer removed from the NiSb surface as a function of etching time for different etchants.

XRD examination was carried out on a DRON-2 diffractometer (CuK_α radiation, λ = 1.5405 Å, diffraction angle from 0° to 55°). The XRD pattern of the material (Fig. 1) showed only peaks characteristic of NiSb. The lattice parameters coincided with those given in the JCPDS PDF.

DTA also confirmed that the samples were phase-pure; the heating curve showed a thermal effect due to melting at 1136°C, in agreement with earlier results [4].

Mass spectrometry data for NiSb samples

Element	at %	mol %	at %	mol %
	sample 1		sample 2	
C	0.040	0.0053	0.039	0.0050
Mg	0.0085	0.0023	0.010	0.0026
Al	0.032	0.0097	0.036	0.010
Si	0.042	0.013	0.055	0.017
P	0.0005	0.0002	0.0004	0.0002
S	0.0023	0.0008	0.0055	0.0020
K	0.010	0.0045	0.0075	0.0034
Ca	0.016	0.070	0.06	0.0075
Ti	0.0005	0.0003	0.0005	0.0003
Cr	0.0012	0.0008	0.0012	0.0007
Mn	0.0025	0.0015	0.0042	0.0026
Fe	0.028	0.018	0.027	0.017
Ni	50.50	32.74	49.95	32.25
Co	0.0015	0.0010	0.0015	0.0009
Cu	0.0007	0.0005	0.0006	0.0004
Zn	0.0005	0.0004	0.0004	0.0003
Sb	49.28	67.19	49.82	67.67

Note: Sample 1 was cut from the first grown portion of the crystal, and sample 2 was cut from the tail end.

Single crystals were prepared by horizontal Bridgman growth in boats made from quartz coated with pyrolytic carbon, alundum, or graphite.

The best NiSb crystals were grown in a pure hydrogen flow using graphite boats 250–270 mm in length and 23–25 mm in diameter, which were mounted in a quartz tube 45–50 mm in diameter. The growth unit included a 600-mm-long two-zone furnace and a drive system for translating the furnace along the boat at a rate of 2–6.5 mm/h. The temperature of the hot zone was 1200–1220°C. In the second zone, the temperature profile sloped down with a gradient of 50°C/cm. The temperature was maintained with an accuracy of ±0.5°C. One of the NiSb crystals grown under such conditions is shown in Fig. 2.

The structure of NiSb single crystals was determined using x-ray intensity data collected on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (graphite monochromator, MoK_α radiation, λ = 0.7107 Å, θ-scan mode). Absorption correction was evaluated from transmission curves. All crystallographic calculations were made using SHELX-93 [6]. The structure was solved by the heavy atom method and was refined by a full-matrix least squares technique with anisotropic thermal parameters.

The refined lattice parameters of NiSb (hexagonal symmetry, sp. gr. $P6_3/mmc$, NiAs structure) are a = 3.953 Å and c = 5.141 Å. Figure 3 shows the structure of NiSb projected along the [010] and [100] directions.

The table presents mass spectrometry data for two samples cut from a single-crystal NiSb ingot, one from the first grown portion (sample 1) and the other from the tail end (sample 2). Note that sample 1 was enriched in Ni, and sample 2, in Sb as compared to the stoichiometric composition. Note also that the effective distribution coefficients of Mg, Al, Si, S, Ca, and Mn are less than unity, and those of C, P, K, Fe, Cu, and Zn are greater than unity.

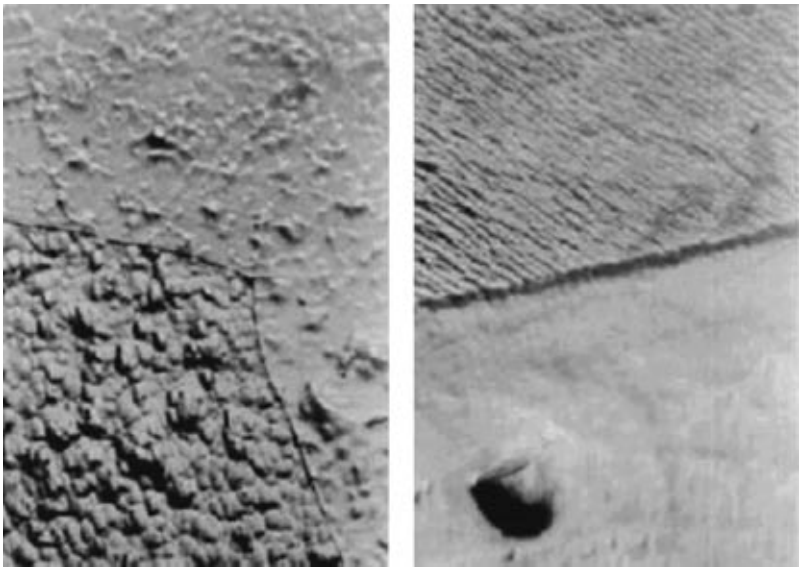

Fig. 5. NiSb surfaces etched with a 1 : 1 mixture of HNO_3 and HF; 200×.

To prepare specimens for microstructural examination and NiSb substrates, we used polishing etchants based on nitric acid. Figure 4 presents 300-K etching rate data for NiSb substrates and different etchants.

Microstructural analysis (EPIQUANT optical microscope) revealed a number of defects on the surfaces of two samples cut from the tail end of one of the crystals (Fig. 5), in particular, pores and small-angle boundaries.

Thus, using Bridgman growth, we prepared large, structurally perfect NiSb single crystals. According to single-crystal XRD results, the lattice parameters of the crystals (hexagonal symmetry, sp. gr. $P6_3/mmc$, NiAs structure) are a = 3.953 Å and c = 5.141 Å. Polishing etch compositions were selected for revealing structural defects and for the preparation of substrate surfaces.

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