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The effect of deposition rate and thermal annealing on morphology and microstructural evolution of Nickel-Bismuth thin film

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ABSTRACT

Bismuth/Nickel thin films were deposited on borosilicate glass substrates using an electron beam evaporator equipped with thickness monitor. Thin film of Bi (10 nm) was deposited on top of pre-deposited Ni (10 nm) film at 0.6 and 1.8 Å/second deposition rates. The samples were then annealed at temperatures between 60 °C and 260 °C for 1 to 5 h under vacuum of $\sim 1 \times 10^{-6}$ mbar. Scanning electron microscopy was used to investigate surface morphology. Scanning electron microscopy images depicted islands at all temperatures including the as-deposited sample. High resolution transmission electron microscopy reveals highly crystalline film and nanowires with energy dispersive x-ray spectroscopy showing that the film and nanowires were formed by Bi and Ni elements with oxygen as impurity. Rutherford backscattering spectrometry revealed intermixing of layers at the interface. Furthermore, spontaneous formation of $NiBi_3$ and NiBi stoichiometry was observed attributed to reaction-diffusion mechanism during deposition. X-ray diffraction revealed structural transformation of the films from amorphous (as-deposited) to polycrystalline hexagonal β-NiBi crystal structure at 60 °C to 200 °C. X-ray diffraction pattern also revealed hexagonal crystal lattice with preferential growth orientation along the [1 0 1] plane with other supported planes [0 0 2], [1 0 2], [1 1 0] and [1 0 3]. The results pointed toward successful utilization of this approach to prepare templates for the synthesis of well controlled, vertically aligned and well distributed crystalline nanowires of Ni-Bi binary system more relevant to the industrial application.

1. Introduction

Ni-Bi bimetallic alloys, NiBi and $NiBi_3$, have received much interest from researchers in the past decade due to their display of interesting magnetic and superconducting properties [1–8]. $NiBi_3$ has been mostly investigated for its superconducting behavior [1–8] while NiBi has also been identified as potential candidate for lead free soldering material for electronics [9–11]. However, in microelectronics devices, the reaction of thin film metallization layer and solder materials at joints is critical and therefore proper care has to be considered when choosing materials to be used [9]. It has also been reported in the literature that low dimensional nanostructures of bi-metallic systems such as Ni-Bi are interesting and of fundamental importance for investigation of classical and quantum size effect that are becoming more interesting and relevant for industrial application [12]. They can be used for single electron devices, optoelectronic devices, magnetic storage devices, and as nucleation sites for nanowires growth, and nanoscale interconnects [12]. In the context of quantum size effect, we chose to investigate the structural formation of Bi and Ni islands to be used as a template for nanowires growth for further magnetic and superconductivity studies.

Various techniques have been employed to synthesize Bi and Ni-Bi bimetallic nanosystems but none of them have used electron beam evaporation. Ion beam mixing has been reported as one of the methods of mixing metallic and semiconductor materials [13–15]. Bin-Kun Wu et al., [16] used RF-sputtering technique to synthesize Bi nanowires while Siva et al., [17] investigated interdiffusion in Ni-Bi bilayers using ion beam mixing method. Chiu and Shih [18] fabricated Bi nanowires on Si substrate using an electron beam writing technique. Other reports suggested co-melted high purity Ni and Bi at high temperature of ~900 to 1100 °C to achieve $NiBi_3$ stoichiometry [19,20].

Other reports [21–25] suggested the use of chemical deposition as a better alternative method to physical deposition especially when it comes to creation of NiBi nanostructures with well controlled dimensions. The difficulty with chemical deposition is the alignment of structures such as nanowires. Some reports [18–20] suggest the use of template for nanowires formation but this method also poses a challenge when it comes to preservation of nanowires during template etching process. Therefore physical deposition has been seen as a viable

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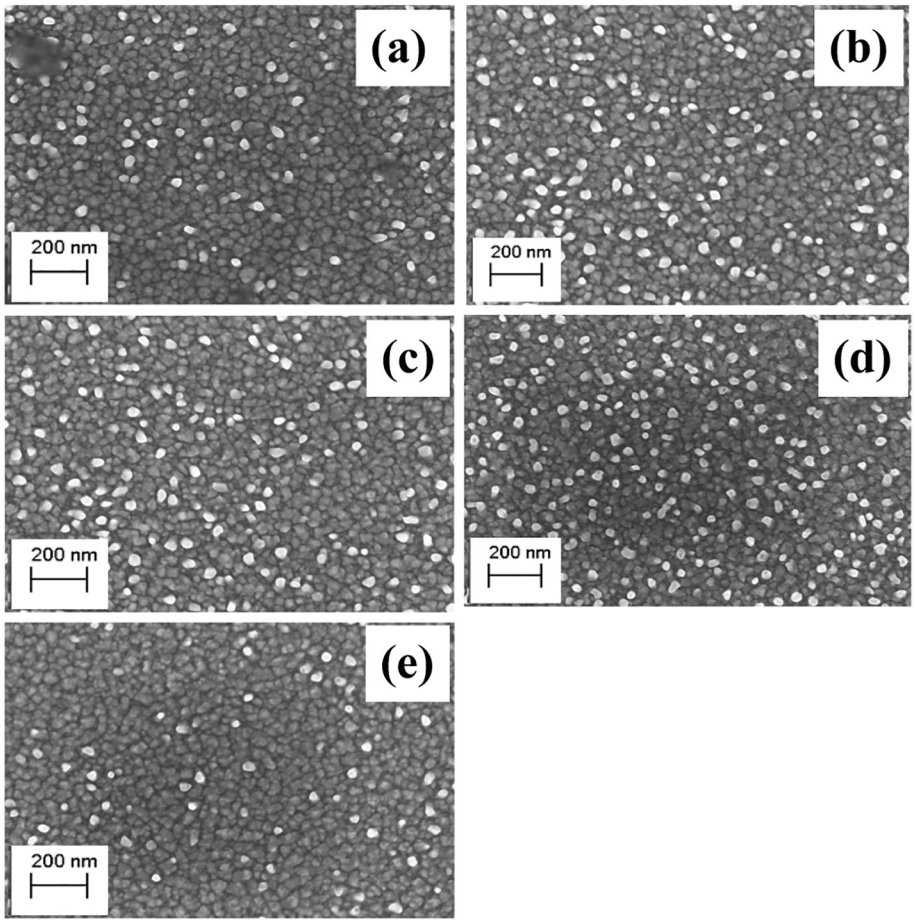

Fig. 1. SEM images of NiBi islands synthesized from as-deposited Bi (10 nm)/Ni (10 nm) films via electron beam evaporator at 0.6 Å/s film deposition rate. Depicted in the figure are (a) as-deposited films and then annealed at (b) 60 °C, (c) 100 °C, (d) 200 °C and (e) 260 °C for 1 h.

method for creation of well aligned nanostructures.

Here we report on effect of deposition rate on the formation of Ni-Bi islands on borosilicate glass substrate synthesized using e-beam evaporation. With this method, the diameter, shape, and density of Ni-Bi islands were tuned by controlling the deposition rate. The effects of annealing at temperatures below Bi melting point are also included in this investigation in order to phase formation and verify the predictions based on the effective heat of formation (EHF) model. The surface modification and formation of islands were studied using scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDX). Interfacial mixing of the layers was investigated using Rutherford backscattering spectrometry (RBS). Crystallinity and phase formation was investigated using x-ray diffraction spectrometer (XRD). All results are presented and discussed.

2. Experimental procedure

Bi and Ni films were deposited onto borosilicate glass substrates using a 3 kW high vacuum e-beam evaporation system at room temperature (RT). Substrates were ultrasonically cleaned, prior deposition, using acetone followed by isopropanol and then dried thoroughly to avoid contamination. Substrates were then mounted on non-rotating substrate holder and transferred into the deposition chamber. Highly pure Bi and Ni pellets (Purity 99.999%) targets were placed in the crucibles for the deposition of Bi and Ni thin films, respectively. The e-beam current and deposition chamber pressure for Ni deposition were 80 mA and 10^{-6} mbar, while same parameters were 50 mA and 10^{-6} mbar for Bi deposition. First batch of samples were deposited at 0.6 Å/s while another batch at 1.8 Å/s. During deposition, thicknesses were monitored using thickness crystal monitor and were kept at 10 nm for both Ni and Bi films sequentially except for only one case where the thickness of Bi was increased to 40 nm. The first batch of samples deposited at 0.6 Å/s were thermal annealed at 60 °C to 260 °C for 1 h respectively to determine the best temperature for crystallization. After determining that at 200 °C the film is highly crystalline with no more improvement above 200 °C, the second batch deposited at 1.8 Å/s were then thermal annealed at 200 °C for 1, 2, 3, 4 and 5 h sequentially to determine the effect of annealing time.

The morphology of the film was studied using a Carl Zeiss Auriga SEM operated at 5 keV using a lens detector equipped with energy dispersive x-ray spectroscopy instruments. High resolution transmission electron microscope (HRTEM JEOL JEM-2100 Fas TEM) equipped with EDX was used for internal structural investigation and elemental composition of the film and nanowires. The surface roughness was determined using a NanoSurf Easycan 2 atomic force microscope (AFM) operating in a non-contact mode. The structure of the as-deposited and annealed samples was investigated using x-ray diffraction XRD diffractometer (Model Bruker AXS D8). The thicknesses and compositions of the as-deposited and annealed samples were measured by Rutherford backscattering spectrometry (RBS) using 2 MeV He^+ ions at KU Leuven University. The samples were individually mounted on a ladder and then loaded into the sample chamber. The channel number calibration in terms of backscattered energy of particles was achieved using gold-cobalt on top of silicon dioxide deposited on silicon substrate ($AuCo/SiO_2/Si$) standard sample. An average current of 40 nA and total charge of 20 μC were used for all samples. The vacuum pressure during measurement was better than 10^{-7} mbar. The energy spectra of the scattered He^+ ions were recorded using glancing angle Si surface barrier detector with energy resolution of ~23 keV positioned at an scattering angle of 111° and the sample surface normal tilted off the beam axis by 10°, away from the detector, to increase the beam path length for better depth resolution. Simulations of RBS spectra were achieved