Fabrication and nanostructure study of ultra thin electroplating constantan film on GaAs as a thermopower sensor

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Abstract. Ultra thin film of constantan was potentiostatically electrodeposited on n-type GaAs (111) from a citrate electrolyte containing both copper and nickel ions. SEM and EDX analyses were used to determine the film quality and composition. In order to fabricate high quality constantan alloy the optimum values of deposition potential and solution temperature were respectively found -1.45 V and 22-26 ºC using the SEM analyses. The SEM images also showed that the grain size of the alloy extremely increases for the films with thickness of above 400 nm.

1. Introduction
Electrodeposition is a very convenient technique for the production of metallic single and alloy films and also for sharp interfaces. This technique has been recently employed in the production of metallic nanostructures with interesting magnetic, mechanical and thermal properties [1]. It takes place at ambient temperature and pressure [2]. Electrodeposited layers can be made much thinner than the standard commercially available extruded foils, enabling an increase of thermo elements in sensors [1, 3, 4]. The aim of this work is to electrodeposit constantan, a solid solution of 35-50 wt% Ni in Cu, from a single electrolyte on GaAs substrate under different growth conditions such as deposition potential, electrolyte temperature, and film thickness.

2. Experimental details
Ultra thin constantan films were electrodeposited onto n-type GaAs (111) substrate (Si doped, thickness is 350µm) using an aqueous citrate electrolyte containing Cu and Ni ions. The bath involved 0.171 mol/l NiSO₄, 0.019 mol/l CuSO₄, 0.190 mol/l C₆H₄Na₂O₇ (trisodium citrate) and deionized water with a resistivity of 18.2 MΩ-cm [5]. The solution pH was measured 4.7. Deposition was carried out potentiostatically in a three-electrode cell. The used substrates were n-type GaAs (111). The substrate surface was rinsed in a 10% NH₄ aqueous solution, to remove oxides and followed by rinsing deionized water [6]. An ohmic contact was made by painting a liquid Ga-In eutectic on unpolished side of the substrate and contacting them to a silver plate as metallic supporter. A square shape exposed area of 25mm² was selected using a piece of Kapton tape. The distance between cathode and anode was 3-3.5cm and reference electrode was placed as near as possible to cathode. The deposition process was computer controlled enabling the current flowing through the circuit to be...
monitored and integrated. A sufficient voltage was applied between cathode and a saturated calomel electrode (SCE) as reference. Once the charge corresponding to the desired thickness (from Faraday’s law) is reached, the applied potential is automatically stopped.

In order to fabricate high quality samples, a series of constantan films was electrodeposited under potentials of -0.5V to -1.7V with 0.1 V steps at room temperature. From the SEM images and EDX analyses the optimum potential was achieved. Another series of such films was also fabricated under the optimum potential from the electrolyte at different temperatures from 17 °C to 50 °C.

3. Results and discussion
Cyclic voltammetry (CV) is a very powerful tool for initial electrochemical studies of a new system and it is very useful for obtaining information about the electrodes reactions and solution potentiodynamic behaviour. Figure 1 shows the CV curve of the electrolyte, as it can be seen when deposition potential varies between -0.2 V and -0.95 V only Cu ions are reduced and for the more negative potential both Cu and Ni ions are spontaneously reduced. This result is also confirmed by EDX analysis (see figure 2).

Ni content of the first electrodeposited series of the constantan films was determined using EDX. Figure 2 shows the variation of the Ni content versus deposition potential. As it can be seen the deposition of Ni starts from -0.95 V. According to this curve the best voltage for growing constantan is around either -1.45 or -1.2 V. In the other hand SEM images of the film grown at -1.45 V has a shiny appearance which indicates a low level of porosity and small grain size. Because the current density is sufficient to achieve an optimum rate of the growth at this potential. A typical SEM image of such film is shown in figure 3. Thus, the optimum voltage was determined as -1.45 V.
At more negative potential the Ni content remains constant (about 40%), but the film quality becomes worse due to hydrogen evolution. A typical SEM image of such films, grown at -1.6V, is shown in figure 4.

Figure 4. SEM image of electrodeposited constantan film grown under potential of -1.6 V (thickness =100 nm).

Since the ion movement is affected by medium temperature, electrolyte temperature could be an important factor during growth process. So in order to find the optimum electrolyte temperature, a series of constantan films was grown under optimum potential (-1.45 V) from the solution with different temperatures. Figure 5 shows current transient of three identical electrodeposited constantan films from the electrolyte at 30, 40, and 50 °C. As it can be seen when the solution temperature rises the current also rises due to increasing ions movement. Therefore, the nucleation process and then the surface roughness are changed. Figure 6 shows the variation of Ni concentration with respect to solution temperature. According the data achieved for the constantan film, the appropriate solution temperature should be between 20-30 °C. Furthermore, SEM images of these samples showed that the film roughness increases when the electrolyte temperature rises to more than 26 °C. Two typical SEM images of such films are shown in figure 7.

Figure 5. Current transient of three electrodeposited constantan films from a solution at different temperatures (V =-1.45 V).

Figure 6. Ni concentration (wt%) as a function of solution temperature (V =-1.45 V).
It was also expected that the quality of constantan film is depend on its total thickness. So another series of constantan films was grown under identical deposition conditions with different total thicknesses. The variation of Ni content with respect to thicknesses of those films is shown in figure 8. Although the curve does not show any significant change in Ni content, but SEM images show an increase in grain sizes and roughness of the films with total thickness of above 400nm. Figure 9 shows such a rough film with 500 nm thick.

4. Conclusion
In summary we have electrodeposited ultra thin constantan film on n-type GaAs (111) using a citrate-based electrolyte. By studying SEM images and EDX analyses of the samples in various potentials, the best voltage for growing constantan was found to be around -1.45 V. Ni content and quality of the films were affected by electrolyte temperature. The optimum temperature of solution for growing constantan film under optimum potential was determined around 24°C. It was also observed that for the thick films (more than 400nm) there occurred an increase in the grain sizes and roughnesses.

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