Physical Characterization of Cu-Ni-P Thin Films aiming at Cu/Cu-Ni-P Thermocouples

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Abstract. Cu-Ni-P thin films have a high-thermoelectric power, which allows the fabrication of very sensitive heat-flux sensors based on planar technology. In this work, (100) silicon surfaces were pre-activated in a diluted hydrofluoric acid solution containing PdCl₂. Following, Cu-Ni-P thin films were chemically deposited using an alkaline chemical bath containing 15 g/l NiSO₄.6H₂O; 0.2 g/l CuSO₄.5H₂O; 15 g/l Na₂HPO₂.H₂O and 60 g/l Na₃C₆H₅O₇.2H₂O at temperature of 80 °C where NH₄OH was added until pH was 8.0. It was noteworthy that the stoichiometric percentages of Ni and Cu vary substantially for immersion times in the range of 1 to 3 min and they become almost stable at 50% and 35%, respectively, when the immersion time is higher than 3 min. In addition, the percentage of P remains almost constant around 17-18% for all the immersion times studied. On the other hand, the sheet resistance also varies substantially for immersion times in the range of 1 to 3 min. Based on the surface morphology, smaller grains with size in the range of 0.02 to 0.1μm are initially grown on the silicon surface and exposed regions of silicon without deposits are also observed for immersion times in the range of 1 to 3min. Therefore, the discontinuities and non uniformities of the films are promoting, respectively, the observed behaviours of sheet resistance and stoichiometry.

Introduction

The construction of thermoelectric sensors using thin films of copper and constantan (Cu and Ni in a roughly equivalent ratio) is highly regarded because of the high energy that produce these alloys [1-3]. Starting from the same principle, we can construct these thermocouples on a silicon substrate through a process known as electrochemical process.

Constantan alloys (CuNi) have a very small thermal dependence (almost zero) on its electrical resistivity, which can be noticed by an almost constancy of its thermal coefficient of resistivity (α = 1x10⁻³ K⁻¹) in the range of 20 to 600°C. This dependency also makes agreement with the almost constant coefficient of linear expansion (α = 13.5x10⁻⁶ -16x10⁻⁶ K⁻¹, for temperature ranging from 100 to 600°C, which is almost exclusively due to the fact that this alloy has a high level of crystalline structure, in the mentioned temperature range. Thanks to the small temperature coefficients and low electrical resistivity of Constantan, it ended up becoming one of the main materials for manufacturing resistors and precision measurements, as well as heating devices [3].

Unlike the already known process of electroplating, where we have a voltage drop between the electrodes of different metals, in the chemical deposition, the reaction occurs because of the particular conditions of pH on the solution, and the temperature at which it is depositing the metal ions present in the solution (in the case of this work, ions of Cu, Ni and P) on the silicon wafer (Si) [4,5].
In the chemical deposition process, anodic reactions are observed (where there is oxidation reactions) and cathodic reactions (where there is reduction reactions) happening at the same time giving rise to a conductive electrolyte solution [5].

This paper proposes the study of the aforementioned alloy deposition through electrochemical process where will be extracted the composition and concentrations from Rutherford Backscattering analysis, sheet resistance of the material from four-probe measurements and the visualization of the surface morphology, besides demonstrating the benefits of the electrochemical process for thin film deposition.

**Experimental**

Si wafers were chemically cleaned by RCA cleaning [6]. The recipe used for the RCA cleaning consisted of two baths: (a) 400 ml H₂O + 25 ml NH₄OH (38%) + 175 ml H₂O₂(37%) and (b) 400 ml H₂O + 100 ml HCl (38%), heated at 90°C, for 15 min. Between each bath, the wafers were immersed in deionized (DI) water for 5 min. Following, Palladium pre-activation were performed immerging samples in an acid solution (0.1 g/l of PdCl₂ and 50 ml/l of HF) for 60 seconds in order to obtain Pd sites sparsely distributed onto the silicon surfaces. Finally, CuNi alloys were chemically deposited onto n-type Si substrates using an aqueous citrate electrolyte containing Cu and Ni sulfates. The solution used was 7.5 g / l NiSO₄.6H₂O, 0.2 g / l CuSO₄.5H₂O, 7.5 g / l Na₂HPO₂.H₂O, 30 g / l Na₃C₆H₅O₇.2H₂O, NH₄OH (pH ≈ 8.0) at 80 °C and thin films were deposited for time immersions of 1, 2, 3, 4, 5, 7 and 10 min.

RBS spectra were taken at 3.0 MeV under normal incidence of a ⁴He⁺ beam and with a scattering angle of 170° using an accelerator Tanden, model 55 DH/NEC. In addition, the SiMRA program [7,8] was employed to adjust a simulated spectrum to the experimental one using fitting of composition and areal concentration (NP(atoms/cm²)) where NP is proportional to the RBS-signal area of the formed composite or element [7]. In addition, the stoichiometric percentage of Ni, Cu and P were obtained by means of the relative values of the areal concentrations.

In addition, the sheet resistance of the films was measured by four-point probe and the surface features of the were observed by Field-Emission Scanning Electron Microscopy (FE-SEM).

**Results and Discussion**

At first, several preliminary tests were performed with different concentrations of NiSO₄, CuSO₄ and Na₂HPO₄ at a fixed pH of 8 and at a fixed temperature of 80 °C. The addition of copper influences the electroless reaction due to the difference in redox potential between Ni and Cu [2].

![Figure 1. Typical RBS spectrum and simulation for a immersion time of 1min.](image)
Copper is preferentially deposited because of its higher reduction potential than nickel and phosphorus. Thus, it was established that a Ni/Cu atomic ratio of at least 70 in the chemical solution to obtain Ni/Cu atomic ratio of 0.5 in the deposits. After the deposition process, the deposited Cu-Ni-P films were analysed by means RBS analysis, which was interpreted by SIMRA v.6 program. Figure 1 shows the typical RBS spectrum and the simulated curve for a immersion time of 1 min. In this case, the Cu and Ni signals are partially superimposed since the atomic masses are close. However, the SIMRA program allows one to separate both contributions by fitting the signals in order to obtain areal concentration and composition. The adjusted curves are illustrated superimposed on the experimental ones and, as a result, errors lower than 5% were obtained during the extraction of the relative areal concentrations for Ni, Cu and P.

In addition, figure 2 also shows the typical RBS spectrum and the simulated curve for a immersion time of 4 min where the Cu and Ni signals become almost entirely superimposed since the area under the Cu-Ni signal (areal concentration) was substantially increased compared to the spectrum shown in figure 1. However, the SIMRA program allowed to separate both contributions by fitting the signals of Cu and Ni.

![Figure 2. Typical RBS spectrum and simulation for a immersion time of 4 min.](image)

![Figure 3. Stoichiometric percentages of Ni, Cu and P as a function of the immersion time.](image)

![Figure 4. Sheet resistance and thickness as a function of the immersion time.](image)
Figure 3 illustrates the stoichiometric percentage of Ni, Cu and P as a function of the immersion time. It is noteworthy that the stoichiometric percentages of Ni and Cu vary substantially for immersion times in the range of 1 to 3 min and they become almost stable at 50% and 35%, respectively, when the immersion time is higher than 3 min. In addition, the percentage of P remains almost constant around 17-18% for all the immersion times studied and the sheet resistance also vary substantially for immersion times in the range of 1 to 3 min. Figure 3 suggests a continuous structural change of the morphology for immersion times in the range of 1 to 3 min.

Figure 5. FE-SEM micrographs of the Cu-Ni-P films for immersion times of: (a) 1 min, (b) 2 min, (c) 4 min, (d) 5 min, (e) 7 min and (f) 10 min.

The sheet resistance was measured by means of the four-point probe technique and, the thickness was estimated by the relation between the reference resistivity for constantan ($\rho: \text{cm}$) [4] and the measured sheet resistance. It was noteworthy that the sheet resistance presents a great change for immersion times in the range of 1 to 3 min, which is closely correlated to the great change of stoichiometry observed in the same range of immersion times. On the other hand, as expected, the sheet resistance is substantially lower for immersion times higher than 3 min. To shed further light on the morphology evolution, the surface features were observed by FE-SEM, as shown in figure 5.
From FE-SEM micrographs presented in figure 5, it is clear that smaller grains with size in the range of 0.02 to 0.1 μm are initially grown on the silicon surface where it is visible exposed regions of silicon without deposits, for immersion times of 1 min and 2 min. Figure 5c already shows a surface without exposed regions for immersion time of 4 min (very similar to the one obtained for 3 min, not shown), which means a great change in the morphology as already pointed out by the results of stoichiometry and sheet resistance. In the following, for immersion times higher than 3 min, the average grain size increased from about 0.1 μm to a upper limit of 0.5 μm when the immersion time achieves 10 min. This evolution of the grain size can be correlated with the concomitant decrease of the sheet resistance from 11.3 to 3.5 Ω/square for the immersion time varying from 3 to 10 min. Therefore, the discontinuities and non uniformities of the films are promoting, respectively, the observed behaviours of sheet resistance and stoichiometry.

1. Conclusions

Cu-Ni-P thin films were chemically deposited using a de-ionized-water-diluted alkaline chemical bath containing 15 g/l NiSO₄·6H₂O; 0.2 g/l CuSO₄·5H₂O; 15 g/l Na₂HPO₃·H₂O and 60 g/l Na₃C₆H₅O₇·2H₂O at a temperature of 80°C where NH₄OH was added until pH was 8.0. The concentrations and compositions of the films were obtained by Rutherford Backscattering (RBS) and the surface morphology was characterized by Scanning Electron Microscope (SEM).

Copper preferentially deposited because of its higher reduction potential than nickel and phosphorus. Thus, it was established that a Ni/Cu atomic ratio of at least 70 in the chemical solution to obtain Ni/Cu atomic ratio of 0.5 in the deposits.

It was shown that the stoichiometric percentages of Ni and Cu varied substantially for immersion times in the range of 1 to 3 min and they became almost stable at 50% and 35%, respectively, when the immersion time was higher than 3 min. In addition, the percentage of P remained almost constant around 17-18% for all the immersion times studied. On the other hand, the sheet resistance also varied substantially for immersion times in the range of 1 to 3 min. Based on the surface morphology, smaller grains with size in the range of 0.02 to 0.1 μm were initially grown on the silicon surface and exposed regions of silicon without deposits were also observed for immersion times in the range of 1 to 3 min. Therefore, the discontinuities and non uniformities of the films promoted, respectively, the observed behaviours of sheet resistance and stoichiometry.

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