NANOSTRUTURAL ANALYSIS AND SIMULATION OF THERMAL ANNEALING OF Ni/Au MULTILAYERS ON Si

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Received 22 October, 2012

Abstract–We deposited three different Ni(20 nm,15 nm)/Au(10 nm,5 nm)/Si(111) multilayers using the dc sputtering method in order to study the nanostructure evolution by X-ray diffraction (XRD) and in situ High Temperature XRD (HT-XRD), with increasing annealing temperature. The nanostructural properties of the Ni/Au contact to p-Si were also investigated during annealing. The Ni/Au/Si contact layers were annealed in situ in vacuum chamber for 180 minute up to 500°C. The Ni layer was in contact with the p-Si before annealing. However, after annealing, the Au layer had diffused from the top layer to the interface. The Au layer on the p-Si surface resulting from the in diffusion of Au atoms during annealing may contribute to ohmic contact formation. Based on the Fuzzy Model Simulation (FMS), we also confirm the behavior of Ni/Au system with increasing annealing temperature.

1. Introduction

Recently, nanostructured materials like compositionally modulated alloys multilayers have become widely studied [1-5]. These materials with bilayer period thickness less than 100 nm have very interesting properties in technology, which are unattainable in bulk materials. Surface and interface structures of these layers have a great influence on many physical properties such as electrical, magnetical, optical and so on. A detailed knowledge of the nanostructural parameters is then crucial.

There are many factors that may determine film structure: lattice mismatch, lattice symmetry, temperature, thickness or coverage, and so on. Depending on the relative importance of each of these factors, the structures of films may be significantly different from those of the related bulk materials. In other hand, for light emitting diodes (LEDs) and laser diodes (LDs), the preparation of low resistance contacts to p-type layers is a rather challenging task. It has been reported that Au/Ni based bilayer structures annealed in an oxygen containing ambient are capable of forming ohmic contacts to p-GaN with a specific contact resistance [5-7]. The images of the structural XRD are a very effective tool to study the structure of thin film due to its good monochromaticity and strong intensity. Since the strong XRD fully penetrate into the film, information on the internal atomic layer structure as well as the buried film-substrate interface is probed.

Electrical contact is made by thermally evaporating Ni/Au on semiconductors and heating the sample to a suitable temperature for a certain amount of time to allow the Ni/Au to melt and diffuse into the heterostructure. A major goal in the annealing process is to minimize the contact resistance. This resistance is largely dependent on the temperature and time spent in the last leg of the annealing process [7-8]. In other hand, metallic multilayered films with artificial superstructures are fabricated by alternately depositing layers such that a one-dimensional composition modulation is
produced. There is a strong interest in modifying physical properties of these materials by controlling before and after growth or annealing procedures. The basis for any understanding of multilayer properties must lie in the structure of thin adsorbate film.

The Ni/Au system is considered as a system and has the following features: (a) both Au and Ni metals have FCC structures. (b) In spite of a large difference in lattice constants ($a_{\text{Au}} = 0.4079$ nm, $a_{\text{Ni}} = 0.3524$ nm and $(a_{\text{Ni}} - a_{\text{Au}})/a_{\text{Au}} = -0.14$), epitaxial growth of Ni films on [001] oriented Au films is coherent if the thickness of the Ni film is less than a critical value [6-8].

Experimentally, in situ Reflection High Energy Electron Diffraction (RHEED) and XRD measurements indicate that Ni grows epitaxially in Au/Ni(100) multilayers [13]. During the growth process, two forms of growth have been formed for less than five monolayers deposited; a pseudomorphic Ni grew (Ni and Au have the same in-plane lattice) and for five or more monolayers, fcc Ni(011) with many twins and stacking faults was present[13].

In this paper Ni/Au/Si multilayers have been produces by using the dc sputtering method in order to study the nanostructure evolution by XRD and in situ HT-XRD, with increasing annealing temperature. Based on the FMS, we also confirm the behavior of Ni/Au system with increasing annealing temperature. The results are a part of investigations of Ni/Au systems in terms of their structural and magnetic properties. With regard to magnetic properties, the multilayer was heated in the passed higher range of temperatures and these systems probably will change coupling from anti-ferromagnetically in ferromagnetically.

The rest of the paper is organized as follows. In Section 2, the experimental procedures are introduced. The concept of fuzzy logic model method and some related works regarding metrics for fuzzy model are reviewed in Section 3. We propose a fuzzy clustering model for fuzzy data with outliers. In Section 4, the results of both experiments and simulation are discussed. Finally, Summary and conclusions are presented in Section 5.

2. Experimental

The Ni/Au multilayers were grown by dc sputtering under high vacuum on a thick Si(111) wafer. Single crystalline $p$-type silicon (111) oriented wafers were used as substrates for deposition. Before the main process, it was suitably treated, rinsed in detergent and acetone and activated in 10% HF and cleaned by the standard procedures used in microelectronics technology. The substrate layer has been annealed at 100°C during 30 min. The samples were capped with a nickel and gold layers. Plasma clean the substrate before deposition has been done for good adhesion. More details on the growth can be found elsewhere [1-5]. Three different samples were synthesized, the bilayers are made of: 20 nm Ni/10 nm Au, 15 nm Ni/10 nm Au and 20 nm Ni/5 nm Au. The thickness was monitored with a quartz oscillator during growth.
Typically, Ni/Au multilayers were deposited under a base pressure of $10^{-6}$ torr and Ar gas pressure of 60 mbar. The substrate to target distance was 0.054 m. Equal number of Au and Ni layers were deposited in all multilayer samples. In general, deposition rates of 1.0 and 1.6 nm$^{-1}$ for Au and Ni targets, respectively, were used in the experiments. We employed a Philips-X, Pert diffractometer with Cu-Ka radiation to carry out the X-ray diffraction experiments. XRD and in situ HT-XRD (Cu-Ka radiation, $A = 0.15405$ nm, Bragg–Brentano geometry) method was used from a sealed tube operating at 45 kV and 40 mA. The samples were step scanned from 35° to 138°, 20, in steps of 0.02° with a count time of 0.2 s/step. A variable slit was employed to illuminate a 1 mm width of the sample. The peak intensities and line widths were analyzed for investigation of structure, phase composition transitions and the texture with increasing annealing temperature.

3. Fuzzy Logic Model Method

An introduction to the fundamental concepts of fuzzy logic has been given in past work [10]. System modelling based on conventional mathematical tools (e.g., differential equations) is not well suited for dealing with theses ill-defined and uncertain multilayer systems. This fuzzy modelling or fuzzy identification, first explored systematically by Takagi and Sugeno [8-9], has found numerous practical applications in control, prediction and inference.

In neural network analysis only quantitative information will be used, but in fuzzy logic qualitative data can be used as well as quantitative information. Some approaches was proposed for fuzzy modelling, here we use a method for constructing rule based on available quantitative and qualitative data. Information used here for fuzzy logic modelling will be placed in two groups: (a) quantitative information from measurements, (b) qualitative information from expert operators. In order to show how well our method works, two simulation experiments are conducted; one in an environment without outliers and the other one in presence of outliers. We almost obtained the same results with both simulation experiments.

3.1. Clustering Fuzzy Data

We now discuss the results of a simulation study carried out in order to compare the performance of our model with existing models able to handle fuzzy data. These models are proposed by Durso and Giordani [10], by Yang et al. [11]. In order to compare the models, bout 2100 fuzzy data sets were randomly generated. After running several models for different values of $q$ and $u$, we chose $q = 1$ and $u = 200$. The other parameters for clustering algorithm were set as follows: number of objects ($n = 10, 50, 100$), number of variables ($k = 2, 8, 16$) and the weighting exponent ($m = 2, 3$). We constructed the data sets in such a way that $c = 2$ patterns can be found all over the simulation. To this purpose, the centers corresponding to the first $n/2$ objects were
generated from the uniform distribution in \([0, 1]\), and those corresponding to the latter \(n/2\) from the uniform distribution in \([0 + 0, 1 + 0]\). All the spreads were generated from the uniform distribution in \([0, 1]\) (case \(\alpha\)). On the other hand, in case \(\beta\), all the centers were generated from the uniform distribution in \([0, 1]\), while the spreads corresponding to the first \(n/2\) objects were generated from the uniform distribution in \([0, 1]\), and those corresponding to the latter \(n/2\) from the uniform distribution in \([0 + 0, 1 + 0]\). \(\theta\) was set to 1.5 and 0.75. In case of \(\theta = 1.5\), the clusters are separated, whereas they are overlapped when \(\theta\) is set to 0.75. Moreover, three sizes of centers with respect to the ones of the spreads were considered by defining a parameter \(h\) having the values \(1/2, 1, 2\). This parameter means that the size of the spreads is \(h\) times that of the centers.

In order to evaluate how our model is able to detect the prototypes in case of possible presence of observations that can be seen as outliers, we added some outliers to cases \(\alpha\) and \(\beta\), mentioned above. After running several models for different values of \(q\) and \(\omega_k\), we chose \(q = 2\) and \(\omega = 200\). The other parameters for clustering algorithm were set as follows: Number of objects \((n = 100, 200, 300)\), where \(n/10\) of them are outliers and the rest of the them are inliers, number of variables \(k = (2, 8, 16)\) and the weighting exponent \((m = 2)\). The modified cases \(\alpha\) and \(\beta\) are as follows:

Case \(\alpha\): The centers corresponding to the first \(\frac{1}{2}\) of inliers were generated from the uniform distribution in \([0, 1]\), and those corresponding to the rest of the inliers from the uniform distribution in \([1.5, 2.5]\). The number of outliers is \(n/10\). The centers of outliers were generated from normal distribution with mean \(= -2\) and variance \(= 2\). The left and the right spreads were generated from the uniform distribution in \([0, 1]\).

Case \(\beta\): The left and the right spreads corresponding to the first \(\frac{1}{2}\) of inliers were generated from the uniform distribution in \([0, 1]\), and those corresponding to the rest of the inliers from the uniform distribution in \([1.5, 2.5]\). The number of outliers is \(n/10\). The left and the right spreads of outliers were generated from Normal distribution with mean \(= 5\) and variance \(= 2\). All the centers were generated from the uniform distribution in \([0, 1]\).

The mean square errors between prototypes obtained by performing our clustering model and the ideal prototypes: It can be observed that mean square errors of the centers are more than mean square errors of left spreads and right spreads in case \(\alpha\), while mean square errors of spreads are higher than those of centers in case \(\beta\). In both cases, small weighting factors \(\omega_k\) (large values for \(1/\omega^k\)) are assigned to data points fitting well to one of the clusters whereas large \(\omega_k\) (small values
for $1/\omega_q^k$ are assigned to outliers. Thus, outliers can be easily identified by their large weighting factors.

4. Result and Discussion

4.1. AFM analysis

The root-mean-square (RMS) roughness values measured with AFM have been determined on areas of 5×5 mm by the nanoscope software. Fig.1 shows AFM images of Ni/Au films obtained at room temperature. The columnar structure was observed in the Ni and Au films deposition on Si(111) at room temperature, a fine grained structure is observed. The significant change of microstructure depending on the deposition temperature can be explained in terms of theories of surface diffusion, grain aggregation and the growth rate of the film. As the deposition temperature increases, the grain size becomes bigger mainly due to the effect of grain aggregation; the species have more time to migrate since the deposition rate becomes lower at this temperature region. So in lower deposition temperature, the surface diffusion is dominant and in higher deposition temperature, the grain aggregation is a main controlling factor. The RMS roughness of Au film was about 3.1 nm. With an increase of the deposition temperature, the surface roughness decreases and shows the minimum value 1.6 nm. At the higher deposition temperature, the surface roughness increases again. It seems that the surface roughness is closely related with the change of the morphology of the layers.

![AFM image of Ni/Au film at room temperature.](image1)

4.2. XRD Analysis

The XRD analysis of the films is shown in Fig.2. In all of coated samples, the results revealed that only diffraction peaks of Ni and Au were presented in X-ray diffraction patterns. X-ray
Thermal Annealing of Ni/Au Multilayers

Diffractograms obtained for Ni/Au multilayer samples grown on Si substrates confirm a well-defined periodic structure of the multilayer. Multilayer reflections are clearly visible, which allows determining the bilayer thickness and structural properties of the multilayer such as preferential crystallographic orientation and crystallite grain sizes. It means that there are no alloying phases in the Ni and Au film. The XRD also revealed that all films are highly textured having Ni(111) and Au(111) orientation. The three other strong diffraction peaks of Au(200), Au(220) and Au(311) are very weak in all of three coated samples. It seems that the Si(111) substrate, which has the strong [111] orientation, lead to the higher degree of preferred orientation of Ni and Au films in our experimental region.

Fig.2. XRD profiles of the as-deposited Ni/Au layers on Si(111).

4.3. HT-XRD Analysis

Fig.3 and Fig.4 show the in situ HT-XRD results as well as fuzzy logic data of the Ni/Au layers annealed at 125°C, 225°C, 325°C and 425°C temperatures, were analyzed for 180 min in vacuum. An insignificant broadening and increase of peak intensities was observed. The recorded peaks were characterized by small half-widths, high maximum intensities and precise symmetries in relation to the axis determining the angular position of the analyzed maximum (Fig.3); no attempts were made to separate them.

From the comparison of (111) reflexes for three multilayers, it was confirmed that the applied proportions of the thicknesses of multilayers did not cause any changes in the integral intensity of the reflex, resulting, however, in its shift. It was found that relative intensity of reflex (111) strongly decreases upon increasing temperature of heated multilayers. In as-obtained multilayers, the relative intensity of the (200) reflex is very low, and only in multilayers heated at 325°C it approaches standard intensities of Au and Ni (I_{(111)} = 100% and I_{(200)} = 46%).

Using the Bragg equation, the values of d-spacing have been calculated. The results of d-spacing and grain sizes after annealing of multilayer have been compared with those obtained for
multilayer which was not heated (Table 1). The trends of changes of \( d \)-spacing in multilayers have been observed independent of Au and Ni contributions. The calculated \( d \)-spacing for diffractions arising from (111) and (200) planes of these systems are also shown. They are presented taking into account changes of about a nonmagnetic spacer. Comparison of \( d \)-spacing determined by experiment with those calculated for a fuzzy logic simulation shows that experimental \( d_{111} \) values for Ni/Au multilayers are higher, while the experimental \( d_{200} \) values are lower than the fuzzy model ones.

![XRD profiles data in comparison of fuzzy logic data of the as-deposited Ni/Au layers on Si(111) before and after heating at a) 125°C, b) 225°C, c) 325°C and d) 425°C temperatures.](image)

Moreover, as is shown in Table 1, the grain sizes connected with Ni(111) reflexes increase upon increasing temperature and for Au(111) decreases. For initial, unheated system \( d_{\text{Ni}} \) and \( d_{\text{Au}} \), the grain size were 17.69 Å and 8.93 Å, respectively. After heating, the grain size values for these multilayers changed to 22.11 Å and 8.51 Å, respectively. The analysis of the \( d \)-spacing connected with the (200) reflexes does not indicate their distinct increase with temperature. For all three multilayers, the intervals between points representing \( d \) values for four temperatures have a nearly identical slope. A deviation from linearity occurs for above 500°C, when first cracks in the multilayers were observed. This may suggest that the similarity of structures explains the facility of formation of solid solutions. The most probable is the formation of a substitutional solid solution in which replacement of atoms by other ones occurs. It is possible that in solid solutions stable over wide range of compositions, some superstructures may be present.
Fig. 4. XRD profile of fuzzy logic data of the as-deposited Ni/Au layers on Si(111) before and after heating at 125°C, 225°C, 325°C and 425°C temperatures for a) 38.26, b) 44.62 and c) 61.75 peaks.
Table 1. FWHM, $d$-spacing and grain sizes before annealing (BA) and after annealing (AA) of Ni/Au

<table>
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<th></th>
<th>FWHM</th>
<th>$d$-spacing, Å</th>
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5. Summary and conclusion

Three different Ni/Au multilayers were synthesized, the bilayers are nominally made of Ni(20 nm)/Au(10 nm), Ni(15 nm)/Au(10 nm) and Ni(20 nm)/Au(5 nm) on Si(111) using MMS in order to study the nanostructure evolution by XRD and in situ HT-XRD, with increasing annealing temperature. At 325°C the multilayers undergo a total deformation and exfoliation from the substrate. The $d$-spacing and grain size of layers differ from interplanar distances in conventional alloys of identical compositions; $d_{111}$ distances are higher and $d_{200}$ are lower than in the alloy. As a result of heating of multilayers in the 200 to 400°C range, Ni/Au solid solutions are formed causing a favored (111) orientation.

Modelling has now a very important position in the development and improvement of new materials for applications. Modelling and simulation techniques affect all stages in the development and improvement of new materials, from the initial formation of concepts to synthesis and characterization of properties. The universal approximation capabilities of the multilayer perception make it a useful choice for modelling nonlinear systems and for implementing general purpose controllers and magnetic characteristics extractor from wide data amount. The results are also simulated based on Wasserstein distance between interval valued data which is generalized to fuzzy data. With the help of this approach, the problem of fuzzy clustering of fuzzy data is reduced to fuzzy clustering of crisp data. The obtained results are very good in comparison of experimental results.

Acknowledgments

This research was sponsored in part by contract No. 89-11648 from University of Arak, Iran.

REFERENCES