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Annealing effects on the electrical resistivity of AuAl thin films alloys

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1. Introduction

Physical properties of thin metallic films and their alloys are a current topic in material science. The knowledge of their physical properties has an impact on metallic interconnections in electronic devices that play a key role in the future of the nanotechnology. Electrical resistivity is an amazing property of the metallic films which depends strongly on the preparation conditions and sample thickness [1–4].

Metallic alloys assume considerable importance in industrial applications where pure metals are widely used. This choice is motivated by the better resistance to corrosion and better mechanical properties suited for the conditions in which they are used [5,6].

The AuAl alloy phase diagram (Fig. 1) can be divided into six principal sections: the first section ranged from 0% to 30% Au as atomic concentration, where AuAl2 is mainly formed. The second section an AuAl5 and AuAl mixture alloy is generated between 30% and 49%. The third section corresponds to identical atomic concentration of Au and Al (50:50). In the fourth section, between 50% and 65% Au, the Au2Al5 alloy is mainly found. In the fifth section, from 65% to 90% Au, Au2Al and Au4Al alloys are formed. Finally, for higher Au atomic concentrations (above 90%) alloys are not formed. Particularly, the AuAl system has been the subject of much research interest due to microelectronic packaging applications [7–10]. The diffusion kinetics formed in this bimetallic film system has been extensively studied by the measurements of changes in optical reflectance [11,12], electrical resistivity [12,13] and mechanical strains [13] during heat treatments. The bimetallic system phase identification has been studied by X-ray [14–16] and electron diffraction techniques [8,15]. The high-energy He+ ion backscattering technique has also been employed [16]. Even on the issue of the diffusion mechanism, researchers have generally assumed that Au is the main diffusing element [13,17] but not clear evidences to support this assumption have been reported.

In the present work, a detailed study of the morphology, crystalline structure, and electrical resistivity of AuAl alloys deposited on Si substrates at different atomic concentrations and different thickness is discussed.

2. Experimental

Al (99.99% purity) thin films (5 mm × 20 mm, area) were deposited on p-type silicon (1 0 0) substrates by thermal evaporation into a vacuum chamber at 10−6 Torr as pressure. Au (99.99% purity) thin film was subsequently deposited on the Al films forming a bilayer. For each case, film thickness was controlled and monitored with a quartz crystal sensor through a MANTEK TM-400 device. Tungsten crucibles were used as heaters for metals evaporation. The deposition rate during growth was maintained at 0.5 nm s−1 approximately. Two groups of Au/Al bilayers were prepared. The first group was prepared varying the Au atomic concentration from 10% to 90%, with 10% steps. In this case, the total thickness of the formed bilayers was always 100 nm approximately. A second group of Au/Al samples were prepared with atomic concentrations of 33:66, 50:50 and 66:33 varying the bilayers total thickness from 100 nm to 250 nm, with 50 nm steps. After deposition, the two groups of bilayers were annealed for 1 h at 400°C into a homemade quartz vacuum oven with Argon flow [18], in order to form the alloys diffusion. The alloy surfaces presented different colorations when the Au atomic concentration increased. Coloration ranged mainly from purple to gray. Purple gold was obtained from 20% to 50% Au, approximately meanwhile gray colorations were presented for higher Au atomic concentrations.
Surface morphology of alloys was analyzed by atomic force microscope (AFM) at room temperature (RT) and scanning electron microscopy (SEM). X-ray diffraction (XRD) was used to confirm the alloy formation at laboratory conditions (22 °C and atmospheric pressure). Grain size was estimated from AFM images taken in surface samples after annealing by using the minimalist method [19]. Energy dispersive spectroscopy (EDS) was used to measure the stoichiometric of the AuAl thin films alloys. The electrical resistivity was measured on different sites of each film surface by means of the collinear four-probe technique.

3. Results and discussions

Fig. 2 shows typical AuAl film alloy morphologies obtained by AFM in contact mode at atmospheric pressure and RT. Image sizes are 1 μm × 1 μm for the two groups of samples. Fig. 2a shows some images of the first group of samples for different atomic concentrations and same thickness (100 nm approximately). Differences in the morphologies can be observed as a result of the annealing processes at 400 °C and the formed alloy (such as segregations). Fig. 2b shows the morphology of the second group of samples deposited with different thicknesses and the same atomic concentration (33:66). Grain size in the second group seems larger than for the first group of samples and increases with thickness.

Table 1 shows the SEM images obtained for 150 nm, 200 nm and 250 nm film thickness for the AuAl samples with 20:80 (Table 1a) and 66:33 (Table 1b) atomic concentration. An identical magnification value (1000×) was used to obtain each SEM image in order to clearly show the different surfaces with the AFM images. Table 1 also shows the corresponding EDS results for each sample. The atomic concentration measured on each film was similar to that initially calculated for film preparation. Segregations were found in the 20:80 samples with thickness, meanwhile the abrupt changes in segregations were found in the 66:33 samples with the increase of thickness. All samples analyzed present similar behavior.

Fig. 3 shows a detailed corresponding EDS analysis for the AuAl (40:60) sample. The atomic concentration measured in this particular alloy was very close to the proposed AuAl alloy. Similar results were found for the other alloy concentrations. This good approximation to the atomic concentration means that the different alloys were formed according to our initial calculations.

Fig. 4a shows the rms-roughness value of the AuAl alloyed films as a function of the atomic concentration. A tendency to increase the roughness value was found from 10% to 50% Au atomic concentration, meanwhile a decrement in roughness was found from 60% to 90% Au atom range. Maximum value in rms-roughness was found at...
Table 1
SEM images and EDS results for the two groups of samples analyzed. AuAl/Si alloys with (a) 20% Au–80% Al and (b) 66% Au–33% Al as atomic concentrations are presented.

<table>
<thead>
<tr>
<th>AuAl (150 nm)</th>
<th>AuAl (200 nm)</th>
<th>AuAl (250 nm)</th>
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<tbody>
<tr>
<td>(a) AuAl/Si alloys for 20:80 atomic concentration. Magnification 1000×</td>
<td>Au (At%): 20</td>
<td>Au (At%): 22</td>
</tr>
<tr>
<td>EDS analysis</td>
<td>Al (At%): 80</td>
<td>Al (At%): 78</td>
</tr>
<tr>
<td>(b) AuAl/Si alloys for 66:33 atomic concentration. Magnification 1000×</td>
<td>Au (At%): 65</td>
<td>Au (At%): 65</td>
</tr>
<tr>
<td>EDS analysis</td>
<td>Al (At%): 67</td>
<td>Al (At%): 65</td>
</tr>
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</table>

50% Au atom. Fig. 4b shows the rms-roughness values of the alloys deposited at different thickness and Au concentrations. A maximum rms-roughness value was presented near 33% Au, meanwhile minimum values were obtained for samples with 66% Au. An increment in roughness with alloy thickness was always found for the alloys at 33%, 50% and 66% Au. This behavior can have an influence in electrical properties of the AuAl alloys, as will be discussed later.

The interdiffusion between Au and Al during heat treatments was confirmed by XRD technique with grazing incidence angle. Fig. 5 shows the XRD results for the formed AuAl alloys (30%, 50% and 60%, Au atomic concentration) after annealing at 400 °C during 1 h. An intermetallic compound was formed instead of the original bilayers of pure metals before annealing. These alloys were compared with standard diffractograms [20]. Al2Au compound was mainly formed for the 30% Au atomic concentration sample. From Fig. 5 the main peaks of this alloy can be seen at (311) and (111) of orientation. On the other hand, AuAl alloys were formed with the atomic concentration 50:50. For this thin metallic alloy the Al2Au main peak (311) decreases, and the AuAl main peaks (011) and (202) increase, meaning an incomplete phase transformation from Al2Au to AuAl. Finally, Au2Al appears for the 60% Au atomic concentration. Main peaks for this sample are (110) and (301). Here, an alloy mixture between Au2Al and AuAl can be observed. The crystallite size was calculated by the Scherrer equation [21] by taking the...
main peak of each diffractogram. The crystallite sizes were 28.1 nm, 27.5 nm and 22.2 nm for 30%, 50% and 60% Au film concentration, respectively. A decrease of the crystallite size was found with the increase of the % Au concentration.

The decomposition of the surface morphology in thin films alloys was analyzed by the minimalist fitting method. This method consists in choosing well-defined elements which are spatially distributed, and allow obtaining a set of parameters to describe the surface shape. The surface roughness and grain size are explicitly expressed in terms of such shape parameters. Fig. 6a displays the grain size behavior as determined from AFM images as a function of the atomic concentration. Values ranged from 95 nm to 175 nm. Minor values in the grain size were found for 10%, 40%, 80% and 90% Au meanwhile an increment was found for 20%, 30%, 50% and 70% Au. A drastic change in grain size can be observed for 40% Au. Fig. 6b shows the grain size as a function of thickness for the 50% Au concentration. A non-linear increment behavior was found in grain size for the thickness increment. In this group, the grain size of the alloys varied from 125 nm to 325 nm. The grain size value and its behavior are similar for the other samples. These behaviors are in good agreement with the results obtained by Mayadas et al. [22] for Al films.

Fig. 7a shows the electrical resistivity behavior as a function of the Au atomic concentration of the AuAl/Si system. A comparison of AuAl system before and after alloy formation is shown. Electrical resistivity of the bimaterial before annealing shows a constant increment with the increase of the Au atomic concentration; however, after the alloy formation, its behavior suffers drastic changes. Minor values in the electrical resistivity were found for the 30%, 70%, 80% and 90% Au after annealing. Major electrical resistivities values were found for the 40% and 60% Au as compared with the electrical resistivity value before annealing. After alloy formation, the electrical resistivity duplicates its value at 40% and 60% Au. The electrical resistivity remains almost constant for the atomic concentration 50:50 before and after the annealing treatment. The Mayadas–Shatzkes model [23] explains that the electrical resistivity in a metallic thin film behaves inversely to the grain size. This behavior can be related to the abrupt changes in the grain size and rms-roughness presented in the alloyed samples. The measured electrical resistivity presents low values for the 30%, 70%, 80% and 90% Au, which also presents low roughness values; meanwhile, for the 40%, 50% and 60% Au, an increment in the electrical resistivity was obtained as well as the corresponding rms values for these concentrations present higher values.

Fig. 7b shows the electrical resistivity as a function of thickness before (inset) and after the heat treatment. Before annealing, the electrical resistivity increases with the decrement of the bimaterial thickness. This behavior is typical for thin films. Similar results in alloyed samples were found after being annealed for 150 nm, 200 nm and 250 nm sample thickness. A notable increment in the resistivity (four times) with thickness 50 nm and 100 nm was probably due to the annealing treatment and to the minor thickness. Nanofilms with thickness below 100 nm, presented higher differences in electrical resistivity meanwhile for films with 150 nm thickness or higher, do not show important changes.
4. Conclusions

We deposited bilayers of Au/Al at nanometric dimensions on silicon substrates in order to form alloys by means of a diffusion process. The electrical resistivity and surface morphology were studied as a function of the atomic concentration and films thickness, respectively. The electrical resistivity and morphological properties of the AuAl alloys presented important differences with Au atomic concentration. Abrupt changes in rms-roughness (grain size) values produce inverse changes in the electrical resistivity. By changing Au atomic concentration we found higher electrical resistivities for 40% and 60% Au concentrations. However, the electrical resistivity remains constant for 50% Au atomic concentration. By changing the alloy thickness the electrical resistivity increases with the decrement of bimaterial thickness, a typical behavior for thin films scale. Only for nanofilms (thickness below 100 nm) the electrical resistivity increases drastically. The behavior of electrical properties found in the AuAl nanoalloys give us a new aspect of the materials in nanoelectronic area. Electrical resistivity is an important property to be considered when interconnections are studied in microdevices.

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