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Structure and Stress in Au/Cu Two-Layer System during Annealing at Different Temperature

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In this work, the Au/Cu two-layer systems, with the total thickness equal to 30 nm are studied. The two-layer systems were deposited by thermal evaporation in a UHV system on the silicon substrate at room temperature. After deposition the samples were annealed. We examined samples subjected to thermal cycle with the different maximum temperature. The X-ray diffraction and X-ray reflectometry are performed for systems before and after annealing. It was found that during the cycle of annealing above 150 °C starts process of penetration of the Au layer by Cu atoms results in alloying. In Au/Cu systems, the final layer is the ordered Au/Cu_3 phase.

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1. Introduction

Devices based on systems consisting of thin layers are widespread in microelectronic technologies. Many physical properties of layered structures are strongly dependent on the stress and structure. Therefore, detailed studies of the relation between the structure and the stress are therefore essential. In particular, the two-layer systems of copper and metal or silicides deposited on semiconductor are very attractive due to a potential use for diffusion barriers and contacts [1, 2]. Recently, there are many studies of the Au/Cu two-layer systems [3–6]. These works are focused on diffusion during thermal annealing and alloying and mechanical characteristic of these systems. Moreover, in ultra large-scale integration devices, some metallization processes are required. As a result, the interconnect lines formed may undergo thermal cycles between room temperature and about designated temperature as subsequent layers of metallization are formed. Therefore, studies of Au/Cu two-layers are very important for achieving stable and long life-time devices.

In this work, the Au/Cu two-layer structures, with the total thickness equal to 30 nm are studied. Experimental observation of the average force F per width w (i.e. F/w) measurements during annealing, X-ray reflectivity (XRR), and X-ray diffraction (XRD) measurements of Au/Cu two-layer systems are presented.

2. Experimental

The Au/Cu two-layer systems were deposited at room temperature by thermal evaporation under UHV. The systems were deposited on 100 μm Si(001) substrates and substrate dimension was always kept at 20 mm × 10 mm. Before the deposition, after standard cleaning in ultrasonic washer in acetone and ethanol, a substrate was dried in nitrogen gas and was immediately loaded into a UHV system. The base pressure in the deposition chamber was equal to 2×10^{-9} hPa. The thickness of deposited layer was controlled by quartz-crystal microbalance.

The process of deposition was carried out with 1 min break between deposition of Cu and Au layers. A break was applied to the relaxation of the copper layer. Both layers Cu and Au was deposited with the constant thickness of 15 nm. Four samples were prepared in the same manner. Three samples were subjected to annealing under vacuum. Samples were horizontally positioned onto annealing table in HV annealing chamber with base pressure 2×10^{-7} hPa. The samples were annealed and cooled with the rate 10 °C/min ranging from room temperature (RT) to 150, 290, and 400 °C, respectively. Temperature was monitored by thermocouple.

Stress in heated thin films was calculated by measuring the change in curvature radius using the Stoney formula [7]. In annealing systems, the scanning laser method described by Flinn et al. [8] was applied *in situ* to the evolution of stresses during annealing. The details of the measurement setups have been described earlier [9]. Change of the substrate curvature during the film growth is proportional to F/w. Positive values of F/w are related to tensile stress whereas negative values — to compressive film stress. However, positive value of a slope of the curve F/w corresponds to tensile incremental stress, even if the average stress is negative. Negative value of the slope corresponds to increase of compressive stress even if the absolute stress value is positive.

The effect of heat treatments on microstructure was studied by X-ray methods. The X-ray diffractometer (PANalytical, Empyrean) was used with Cu K_α radiation (λ = 0.15418 nm) at 40 kV and 30 mA. Samples were studied by X-ray reflectometry and X-ray diffraction in $\theta-2\theta$ geometry.

3. Results and discussion

Figure 1 shows the evolution of stress versus temperature for Au/Cu bilayers in thermal cycles for the

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maximum temperature of annealing: 150, 290, and 400 °C, respectively. In all cycles, the linear changes of stress in compressive direction from RT to about 75 °C are observed. Generally, the strain is the sum of plastic and elastic strains. However, in low temperatures the main role plays only elastic strain. In all samples, as long as the system behaves elastically the stress evolution is a linear function of temperature. Next, the data deviate from straight line. A nonlinear evolution of the stress as a function of the temperature is the result of different plastic deformation processes occurring in the films [9]. During cooling the films contract more than silicon substrate which results in a stress evolution in the tensile direction with the exception of the system subjected to heating to 290 °C. For this system the stress returns to initial value. Restoring the initial value of stress suggests that the system deposited on the substrate has changed its elastic properties in comparison to the system before annealing.

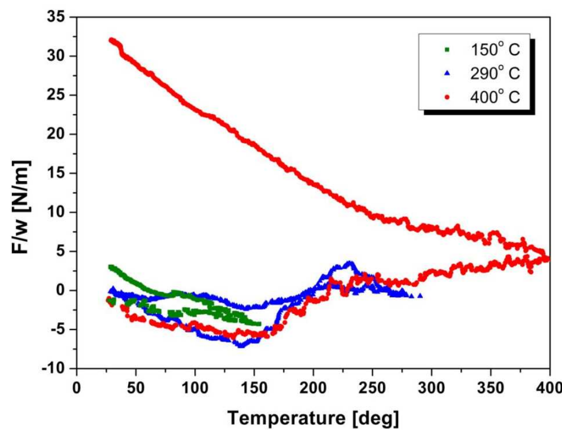

Fig. 1. The total force per unit width F/w dependence on temperature during annealing and cooling the Au/Cu two-layer system in range of the room temperature and 150, 290, 400 °C, respectively.

TABLE I

Data obtained from fitting the X-ray reflectometry curves.

Layer	Density [g/cm^3]	Thickness [nm]	Roughness [nm]
	RT		
Au	18.72	19.6	1.29
Cu	9.42	8.7	1.19
	max. temp. 150 °C		
Au	17.72	19.9	1.17
Cu	9.89	10.2	1.12
	max. temp. 290 °C		
Au	16.64	21.9	0.91
Cu	15.39	7.5	0.76
	max. temp. 400 °C		
Au	16.41	31.7	1.45
Cu	18.31	0.3	0.64

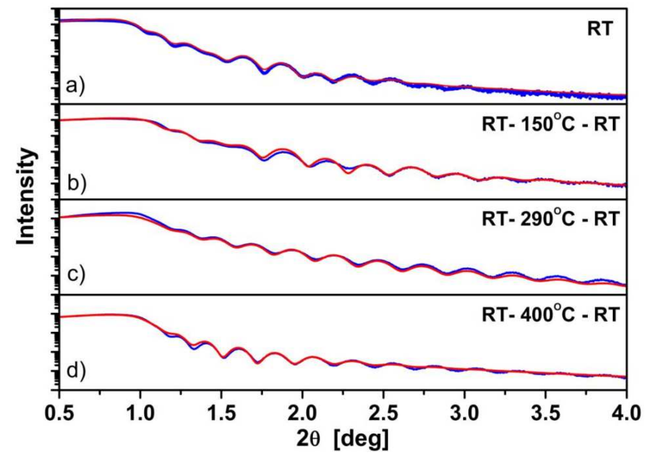

Fig. 2. X-ray reflectometry measurements (blue lines) and fitting curves (red lines) for Au/Cu (a) before and after annealing and cooling in range of the room temperature, and (b) 150 °C, (c) 290 °C, and (d) 400 °C, respectively.

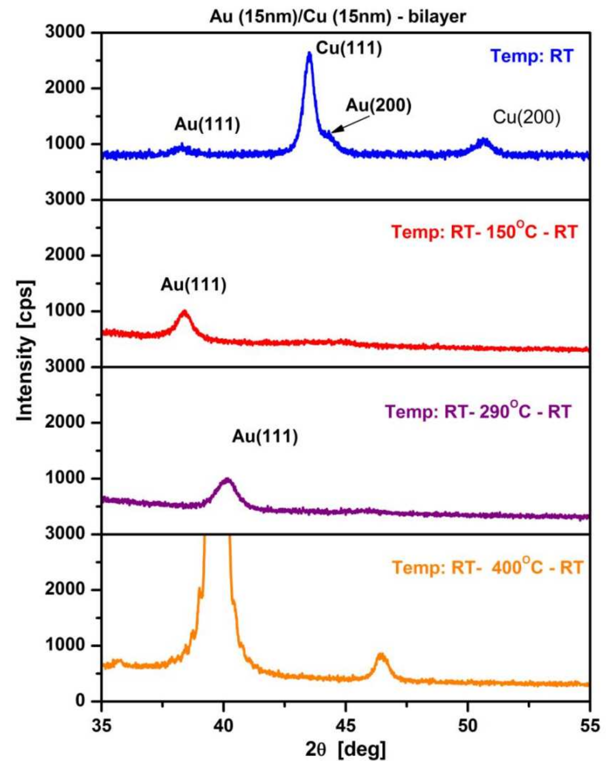

Fig. 3. X-ray diffraction measurements for Au(15 nm)/Cu(15 nm) bilayer (a) before and after annealing and cooling in range of the room temperature, and (b) 150 °C, (c) 290 °C, and (d) 400 °C, respectively.

Figure 2 presents the X-ray reflectometry curves and fitting curves obtained for Au/Cu two-layer systems before and after annealing at 150, 290, 400 °C, respectively. For all samples the characteristic oscillations of the intensity are well detectable. The parameters obtained from fitting X-ray reflectometry curves are presented in

Table I. From fitting of the XRR curves the resulting value of Au layer thickness increases with rising the maximum annealing temperature. In contrast, the density decreased with increase of the maximum annealing temperature. The opposite situation is for Cu layer. For the Au/Cu system heated to of 400 °C, the thickness of the Au layer with a reduced density corresponds to the total thickness of the system and Cu layer shrinks to zero thickness. This result suggests that, in place of the two-layer system, there is formed a single-layer system. This layer is an alloy resulting from the materials of deposited layers. In the order to study formed layer XRD measurements were carried out.

The $\theta-2\theta$ X-ray diffraction profiles for as deposited and annealed Au/Cu two-layer systems are shown in Fig. 3. In the XRD profiles obtained for as deposited Au/Cu system (Fig. 3a), one can distinguish peaks at $2\theta = 38.20°$, $44.28°$ from structure of Au layer and peaks at $2\theta = 43.46°$, $50.57°$ from structure of Cu layer. High intensity of Cu (111) peak compared to Cu(200) peak indicates preferred [111] orientation of the Cu layer. But, weak intensity of peaks from the Au layer suggested a large disorder in gold layer. For system annealed to 150 °C one can see increase of intensity of Au(111) peak and complete lack of Cu peaks. This suggested increase of crystalline order in Au layer and increase of disorder in Cu layer and that in the system exists a large volume of disordered structure. However, for systems annealed to 290 °C and 400 °C one can observe peak approximately at $2\theta = 40.0°$ and $46.4°$ (Fig. 3d) from $AuCu_3$ phase [5] formed during annealing. This also confirms the results obtained from fitting the X-ray reflectometry profiles. This confirms that the area of interface can be treated as a new layer that forms during the annealing cycle, and is consistent with the results obtained by Benazzouz et al. [10] for the Au/Cu systems.

4. Conclusions

From the results of this study of Au/Cu two-layer systems presented here the following conclusions can be drawn:

1. During the annealing the process of penetration of the Au layer by Cu atoms starts above 150 °C and results in alloying.

2. For temperatures lower than 290 °C annealing results in disordered structure alloy structure.

3. Above 290 °C the Au/Cu bilayers form ordered $AuCu_3$ alloy.

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