

In Situ Electron Microscopy Investigations of Solid-State Synthesis in Al/Au Thin Bilayer Films

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Abstract—In situ transmission electron microscopy investigations of solid-state synthesis in Al/Au thin bilayer films are conducted. The samples are heated in the column of a transmission electron microscope. The heating temperature is changed from room temperature to 300°C with a heating rate of up to 120°C min⁻¹. It is found that solid-phase synthesis starts at ≈100°C. At 140 ± 5°C, two crystal phases, Al₂Au (*Fm3m*) and AlAu₂ (*I4/mmm*), are simultaneously observed, while at 235 ± 5°C and higher (up to 300°C) only Al₂Au phase is detected.

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INTRODUCTION

Interaction between gold and aluminum is of great theoretical and practical interest due to the many applications of these elements in microelectronics. Solid-phase synthesis on a boundary between aluminum and gold (Al/Au) takes place at rather low temperatures of ~100°C [1–3]. This results in the formation of Al–Au phases that could substantially differ from the initial Al/Au state in their electrical and mechanical properties. This must also be taken into consideration when devices are used in which aluminum and gold are in direct contact with each other.

The Al/Au thin bilayer films studied in this work were obtained via electron beam evaporation using an MED-020 high vacuum metal evaporation coater (Bal-Tec), with a base vacuum of 5 × 10⁻⁵ Pa. The films were prepared by depositing gold and aluminum layers onto a substrate; thin amorphous carbon films ~10 nm thick on the electron microscope's supporting grid was used as substrates. The thickness of the films during deposition was controlled with a quartz resonator (QSG 100 module); the average rate of deposition was 0.2–0.3 nm s⁻¹. In the investigated Al/Au films, the thickness of the aluminum layers was 44 ± 1 nm; that of the gold layers, 30 ± 1 nm. The layers' thicknesses were chosen so that the atomic ratio Al : Au was approximately 3 : 2. Our studies of microstructures and the phase and elemental composition of Al/Au films were performed on a transmission electron microscope with electron diffraction and by energy dispersion spectroscopy on a JEOL JEM–2100 transmission electron microscope equipped with an Oxford Inca X-Sight energy dispersion spectrometer. Elemental analysis showed that the samples of the investi-

gated films contained 58.5 ± 0.5 at % of aluminum and 41.5 ± 0.5 at % of gold.

The film samples were heated directly in the column of a JEOL JEM–2100 transmission electron microscope equipped with sample holder capable of controlled heating from room temperature to 1000°C (a Gatan Model 652 double tilt heating holder). The Al/Au films were heated from ambient temperature to 300°C (heating rate, up to 120°C min⁻¹), along with simultaneous registration of electron diffraction patterns (using a Gatan UltraScan 1000 CCD digital high resolution camera) and the measurements of the sample temperatures. Our electron diffraction patterns were decoded using the Gatan DigitalMicrograph program; the ICCD PDF 4+ [4] and Pearson crystal structure databases [5] were employed to decode the electron diffraction patterns.

The electron microscopy investigations of the Al/Au bilayer films in their initial state showed that the films were composed of crystals with average sizes of 15 ± 5 nm (Fig. 1a). The diffraction reflections in the selected area electron diffraction (SAED) pattern in Fig. 1b have polycrystal form in the range near 1 μm and correspond to a face-centered cubic (FCC) lattice. Such a structure is typical for both aluminum and gold; since the parameters of the lattices of Al (*Fm-3m* space group, *a* = 4.0494 Å) [6] and Au (*Fm-3m* space group, *a* = 4.0786 Å) [7] differ by only 0.7%, however, it is actually impossible to distinguish between the Al FCC and Au FCC phases via electron diffraction. The electron diffraction reflections of Al and Au phases overlap, resulting in only a slight broadening of detected diffraction reflections.

The thin-layer samples were heated in two steps. Figure 2 shows the curve of temperature changes in a

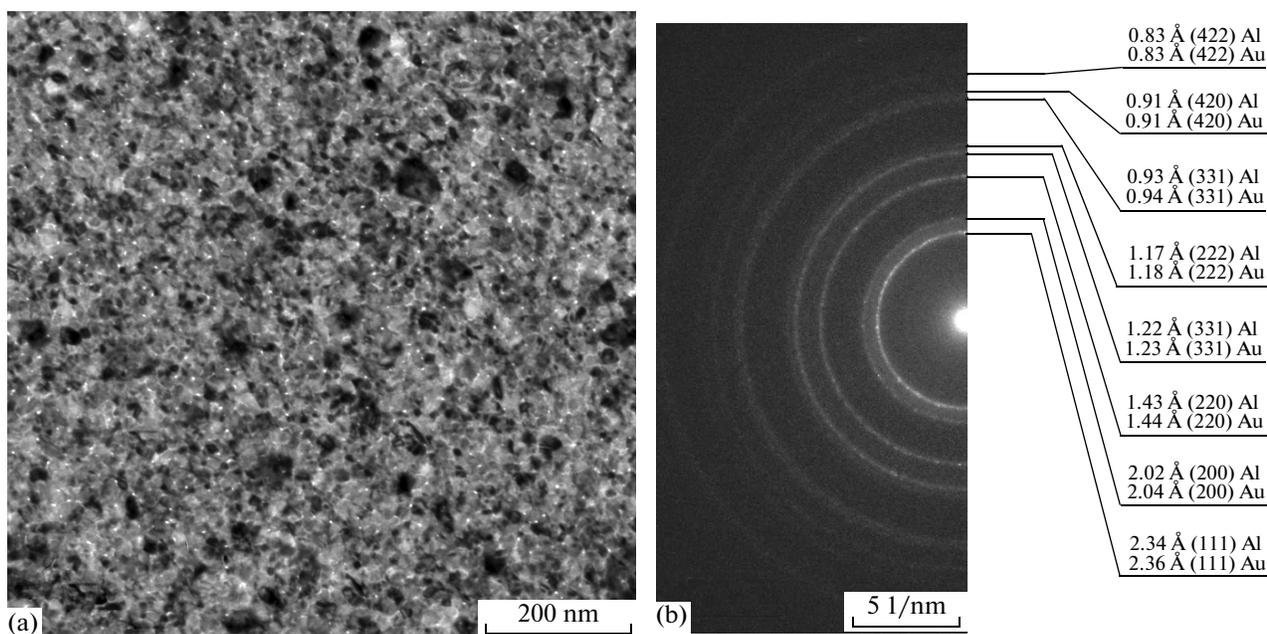


Fig. 1. (a) Electron microscopy image and (b) electron diffraction pattern obtained for the initial state of the Al/Au film.

sample during heating. The first step includes heating to 200°C (heating rate, up to 120°C min⁻¹) accompanied by the brief (≈80 s) annealing at 200°C and cooling to room temperature. At the second step, the samples were heated to 300°C (heating rate, up to 120°C min⁻¹) with brief (≈80 s) annealing at 300°C and cooling to the ambient temperature.

The beginning of solid-state synthesis at the boundary between gold and aluminum layers was detected at $T = 100 \pm 5^\circ\text{C}$ (point 1 in Fig. 2). We can see the formation of diffraction reflections in the electron diffraction pattern that are not typical of pure phases of gold [6] and aluminum [7]. Unambiguous identification of the forming phase (or phases) is prevented by the low intensity of the diffraction reflections, making it impossible to determine the corresponding atomic interplanar distances with accuracy.

When the temperature reached $T = 140 \pm 5^\circ\text{C}$ (point 2 in Fig. 2), there was a qualitative change in the set of diffraction reflections and their intensities in the electron diffraction patterns. In the electron diffraction pattern recorded at $T = 140 \pm 5^\circ\text{C}$ (Fig. 3a), we can see the full set of diffraction reflections typical of AlAu₂ phases (*I4/mmm* space group, $a = 3.349 \text{ \AA}$, $c = 8.893 \text{ \AA}$) [8] and Al₂Au (*Fm-3m* space group, $a = 5.997 \text{ \AA}$) [9]. Based on the analysis of the relative intensities of diffraction reflections we may assume that phase AlAu₂ quantitatively dominates over phase Al₂Au.

Upon further heating to 200°C, a gradual increase in the relative intensities of the diffraction reflections of the Al₂Au phase is observed, relative to the AlAu₂ phase. After brief annealing at 200°C (point 3 in Fig. 2), the quantities of AlAu₂ and Al₂Au phases are

approximately equal and do not change qualitatively as the film's temperature falls to ambient.

Upon reheating (Fig. 2), there is a gradual reduction in the intensity of AlAu₂ diffraction reflections in the electronograms above $T = 60^\circ\text{C}$. When the temperature reaches $230 \pm 5^\circ\text{C}$ (point 4 in Fig. 2), only Al₂Au diffraction reflections are observed in the electron diffraction patterns (Fig. 3b). When the temperature is further enhanced to 300°C with subsequent brief annealing and cooling to room temperature, no changes of diffraction reflections in electron diffraction pattern are detected. The electron microscopy image in Fig. 4, obtained from Al–Au film after annealing at 300°C and cooling to ambient temperature (point 5 in Fig. 2), shows the average crystallite size of Al₂Au phase to be $35 \pm 10 \text{ nm}$.

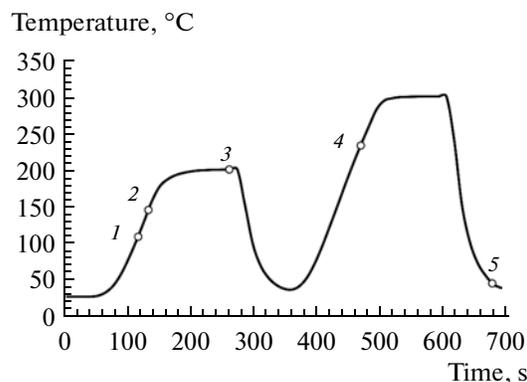


Fig. 2. Curve of Al–Au film temperature changes during in situ heating.

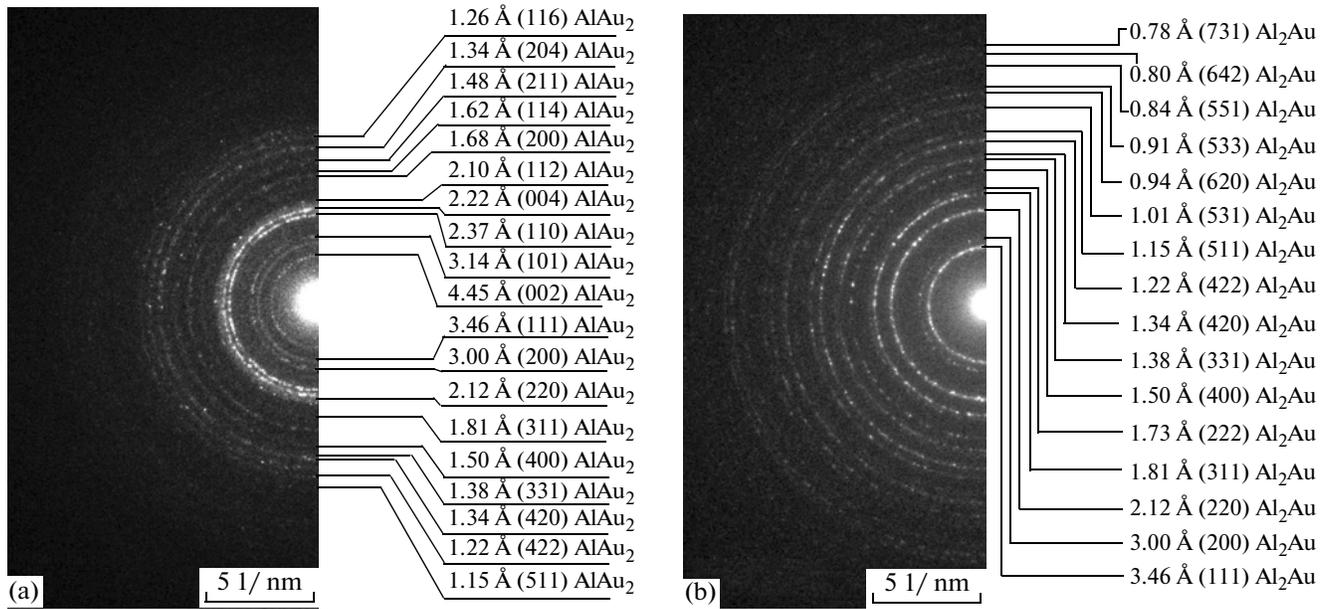


Fig. 3. SAED patterns of Al–Au film obtained at (a) $T = 140 \pm 5^\circ\text{C}$ and (b) $T = 230 \pm 5^\circ\text{C}$.

It should be pointed out that in [1], the formation of AlAu_2 I was observed after annealing at 80°C . Al/Au bilayer films (the Al thickness varied from 5500 to 500 Å, while that of Au was in range of 1000 to 2400 Å) have been studied; but in contrast to this work, in which the rate of film sample heating was up to $120^\circ\text{C min}^{-1}$, the authors of [1] annealed the sample at a fixed temperature for 15 min, with no Au_2Al phase formation being observed after annealing of an Al/Au sample with a thin Al layer (500 Å) at 80°C .

The beginning of the solid-phase reaction in our films was found to occur after heating the Al/Au thin film system to $T = 100 \pm 5^\circ\text{C}$; at this temperature,

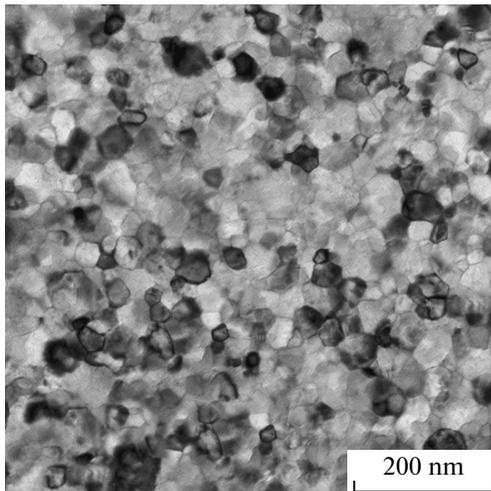


Fig. 4. Electron microscopy image of Al/Au film obtained after heating to $T = 300^\circ\text{C}$ (point 5 in Fig. 2).

however, the reaction proceeds only in a thin layer on the boundary between aluminum and gold. The obtained experimental data allow us to suggest that further heating of Al/Au films leads initially to the formation of AlAu_2 phase ($I4/mmm$ space group, $a = 3.349 \text{ \AA}$, $c = 8.893 \text{ \AA}$) [8] and then to Al_2Au ($Fm-3m$ space group, $a = 5.997 \text{ \AA}$) [9]. This is in qualitative good accordance with the sequence of phase formation predicted in [10, 11]:



Nevertheless, the formation of intermediate Al_2Au_5 , AlAu_4 and AlAu phases reported by other researchers [1–3, 12–14] was not detected in solid-phase synthesis. The absence in this work of the full sequence of phase formation predicted in [10, 11] and observed in [1–3, 12–14] could be explained in two ways. On the one hand, thick films ($\sim 1 \mu\text{m}$ or more) or massive materials with annealing times at fixed temperatures of several tens of minutes [1] to several days [14] or even months. During solid-phase synthesis via the rapid heating of films only several tens of nanometers thick, only some Al–Au phases are likely to be formed.

The second reason for the incomplete sequence of Al–Au phase formation in this work is likely to be the manner of registering the electron diffraction picture: the exposure time of each electronogram was 2 s, while the time between exposures required for information to be read out from the digital camera and saved to the computer's hard disk was 6 s. The high rate of heating and the presence of time gaps (when there was no registration of electron diffraction patterns) would seem to be responsible for the missing intermediate Al–Au phases in our experiments.

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