Effect of Oxide Coverage on the Growth of Amorphous Al₂Pt Phase on an Al Surface

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Abstract. In the present experiments the high temperature successive deposition (HTSD) of Al and Pt and the half shadowing technique producing wedge shaped area with increasing quantity of deposited Pt are applied for studying the initial stages of solid phase reaction producing amorphous Al₂Pt phase. The nucleation of Al₂Pt phase results in a decoration pattern which could be related to the characteristic local oxide coverage of the Al crystal surface developing by kinetic segregation of oxygen species during the Al film deposition. In the area of larger amount of deposited Pt, where the Al₂Pt phase is continuous Kirkendall voids are present.

The samples were investigated in plane by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) and analysed by energy dispersive X-ray spectroscopy (EDX).

Key words: Al–Pt; amorphous phase; TEM; Kirkendall voids.

In the Al–Pt thin film system one amorphous and 11 intermetallic phases are known [1]. For understanding the physics and chemistry of the formation of amorphous and intermetallic phases one has to know whether there are preferential sites due to the local structure and chemistry of surfaces (interfaces) for the nucleation of the various phases and how the parameters and the surface (interface) conditions are controlling the kinetics of the solid state reaction. The solid phase reactions in the Al–Pt thin film system have been studied and reviewed in the literature in various aspects. These are combination of ion mixing and heat treatment of multilayer samples [2, 3], cold rolling of spirals of wounded Al and Pt ribbons [4], rapid solidification [5], temperature annealing of multilayer thin film systems [6–8] and high temperature successive deposition of Al and Pt [9, 10].

In the present work the effect of the surface conditions of Al thin films on the nucleation and growth of amorphous Al₂Pt phase have been studied by HTSD [9]. It is known that in real experiments the environmental oxygen has a strong effect on the growth of Al crystals [11–13]. The co-depositing oxygen segregated to the growth surface by the kinetic segregation develops local covering layers preferentially at the edges of crystals and at bunches of growth steps.

The aim of the present work was on the one hand to investigate the influence of this surface oxide coverage on the nucleation and on the other hand to investigate the phenomena in the post nucleation stage of the solid state reaction. The investigation of these two phenomena has been squeezed in one experiment by applying the half-shadowing technique.

Experimental

The Al–Pt thin films were prepared in an UHV system. The components were evaporated by e-beam sources from graphite crucibles. The deposition rate of Al and Pt were 1 nm/s. The Al and Pt evaporation sources were arranged below the sample holder for producing wedge-shaped part of the sample in the half shadow area [14, 15]. During the deposition 250°C substrate temperature was used as the reaction temperature for developing the amorphous Al₂Pt phase. The samples were prepared on amorphous carbon layer supported by TEM microgrids and air cleave mica. The thickness of Al films (deposited at first) was 100 nm in the whole sample area, while that of Pt deposited in the second step varied between 0 and 2.5 nm in the half shadow area and it was constant (2.5 nm) in the central part of the sample.

A Philips CM20 analytical transmission electron microscope was applied to investigate the samples in plan view. The local composition of the samples was analysed by energy dispersive X-ray
microanalysis (EDX) with a Noran HPGe detector and Voyager system.

Results and Discussion

Central Part of the Sample

In that area the deposited Pt had homogenous thickness of 2.5 nm. The developed amorphous Al2Pt phase formed a continuous layer on the Al crystal surfaces. It has however also a decoration like pattern. Figure 1 shows the representative image of this area and a selected area electron diffraction pattern (SAED) taken from an Al single crystal with the beam direction [011]. The Al film is decorated by Kirkendall voids bound by well-developed crystal faces. The crystals of the Al film are practically randomly oriented. The SAED pattern shown in Fig. 1b proves the existence of the amorphous Al2Pt phase. The EDX analysis of the Kirkendall void area indicated the composition of Al2Pt phase.

Wedge Shaped Area

This area contains the whole growth process of the a-Al2Pt phase from the nucleation up to the development of the continuous layer. In the area where very low quantity of Pt was deposited the nucleation pattern can be seen (Fig. 2). The nuclei are randomly distributed within the single individual crystal surface areas. This indicates that no active nucleation sites related to some surface structural features exist. Some grain boundaries are however decorated by nuclei while others not. This shows that grain boundaries of different surface conditions exist in the Al film. The first type of grain boundaries can be considered as pure ones while the others are contaminated by the segregated oxygen [11–13]. The same phenomenon has been detected in the HTSD experiments carried out on Al–Au system [16–19].

In the area where higher quantity of Pt is deposited very pronounced decoration patterns can be found (Fig. 3). Here again two characteristic types of grain boundary areas are to be detected: the surface areas of one type are empty (A) while the others area decorated by the developed phase (B). The decoration patterns are generally composed of the chains and islands (groups) of grains. There is however surface areas covered by larger flat islands of the amorphous Al2Pt phase (C). These large flat islands contain in most case voids of various sizes.

In the area of further increased Pt quantity the decoration patterns is conserved, however Kirkendall voids shown up simultaneously as described in the previous section. The decoration pattern has continuity in the areas of Kirkendall voids.

The two types of the growth forms of the amorphous Al2Pt phase can be related to the existence of different surface areas of the Al film. One type the flat islands can be related to the smooth and pure terraces of crystal faces (in case of Al the (111) or (100) faces). On these areas lateral growth of the amorphous Al2Pt grains as well as their solid phase coalescence are not limited by any impurity (oxide) phase. That is why large flat amorphous Al2Pt islands can be found. The voids in these islands can be related to the presence of oxide domains, which could be developed on the Al crystal faces before starting the Pt condensation. The same phenomenon has been found in UHV TEM experiments in Al–Au system [17, 18].

Fig. 1. TEM image (a) and SAED pattern (b) of Al–Pt thin film. The SAED pattern taken from an oriented Al grain (SAED size 0.5 μm, beam direction [011]). The diffraction patterns were analyzed by “ProcessDiffraction” computer program [20].