Development of texture and morphology in Cu-Ag thin nanocomposite films on Si

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Cu-Ag films were deposited in vacuum of $10^{-5}-10^{-6}$ mbar onto freshly cleaned Si wafers. The composition of the films corresponded to Cu, Cu$_9$Ag$_1$, Cu$_4$Ag$_6$ and Ag. The films were investigated by X-ray diffraction and pole figures of $<$111$>$ and $<$100$>$ directions were recorded. TEM and XTEM were used to determine the morphological properties of the films. We found that Ag modifies the interaction of Cu with the Si substrate. Low amounts of Ag are enhancing the formation of the biaxial $<$100$>$ texture of Cu. Larger amounts of Ag result in the formation of $<$111$>$ wire texture of both Ag and Cu components.

1. Introduction
The formation and morphological development of two phase composite films still has a number of open questions. E.g. metal–metal (nano)composites are posing many unsolved growth problems. Especially the basic processes of morphological and texture development in them needs to be further clarified [1, 2, 3].
The Cu-Ag system can be a suitable model for the investigation of texture and morphology development in metal-metal nanocomposites. For this purpose Cu and Cu-Ag films grown on (100)Si substrate have been investigated.

2. Experiments
Films of 50 and 400 nm thickness were prepared by co-deposition of thermally evaporated Cu and Ag in vacuum of $10^{-5}-10^{-6}$ mbar onto cleaned (in 10% HF) (100)Si wafers, held at room temperature. The composition of the films corresponded to Cu, Cu$_9$Ag$_1$, Cu$_4$Ag$_6$(eutectic) and Ag in agreement with the physical and morphological properties of these films [4]. The deposition rate of the films was set to 1nm/s. The films were investigated by X-ray diffraction, where pole figures of $<$111$>$ and $<$100$>$ directions were recorded. TEM and XTEM were used to determine the morphological properties of the films.

3. Results and discussion
Thin (20 nm) Cu films grow on amorphous C substrates without any measurable texture according to electron diffraction investigations [5]. In that case oxide formation on the growing Cu crystallites has been considered to be the reason for blocking the selection processes like coalescence, crystal growth and grain growth, supposing that nucleation occurs in random orientation on amorphous substrate [2].
A thin film of Cu grown on (100)Si displays very faint or practically no texture as long as the thickness is 50 nm. The pole figure shows weak intensities in the distribution of both <111> and <100> directions at different angles of inclination to the surface normal (Figure 1a). The evaluation of these intensity distributions is possible in terms of weak, simultaneously occurring textures of <111>, <100> and <110> at least, however, other components cannot be excluded either. It would be difficult to draw conclusions on the biaxial nature of these faint textures from the pole figure. However, crystallographic considerations suggest, that epitaxy of Cu on (100)Si occurs resulting in biaxial <100> texture. The film shows columnar morphology according to zone II structure [2] with a grain size nearly equal to the film thickness. This must be due to the effect of the substrate, providing much less oxygen or water species in the starting stage of the growth process compared to a carbon substrate [5]. Nevertheless, an important role in hindering texture formation in this film can be attributed to the native oxide forming on the Si surface during exposure to air after cleaning and before evacuation. The possibility of epitaxy involves the breaking up of the oxide layer on Si surface by Cu at room temperature as could be evidenced by TEM investigations. The presence of excess oxygen in the samples at the film (Cu) - Si interface was measured by ERDA (Elastic Recoil Detection Analysis).

In Cu/(100)Si films grown to 400 nm thickness a strong \{100\}Cu||(100)Si and <100>Cu||[011]Si biaxial texture appears (Figure 1b). This texture is the result of the selection processes leading to the strengthening of the weak <100>-texture detected in the thin sample (Figure 1a). The selection takes place due to the interaction of the growing grains with oxygen and copper-oxide formation. As described for Al [6], oxide formation blocks the growth of \{111\} facets because of the formation of a covering oxide layer, however, \{100\} facets can keep growing because oxygen can penetrate the crystal in <100> directions more easily than across the densely packed \{111\} planes [7]. The selection processes occur during crystal growth resulting in grain size of a few μm and zone II type structure (Figure 1c).

![Figure 1. <111> pole figures of Cu films of 50 nm thickness (a), 400 nm thickness (b) and TEM bright field cross section image of the 400 nm thick film (c).](image1)

![Figure 2. <111> pole figures of Cu 10at%Ag films of 50 nm thickness (a), 400 nm thickness (b) and TEM dark field cross section image of the 400 nm thick film (c).](image2)
Cu and Ag are practically immiscible according to their equilibrium phase diagram; consequently, we are expecting the formation of a composite film consisting of Cu and Ag crystallites. Ag is a surfactant for Cu, which can affect growth and surface diffusion processes of the growing Cu crystallites without being substantially incorporated into them [8]. Consequently, changes in growth morphology and texture development compared to Cu films can be expected.

Co-deposition of 10 at% of Ag to Cu results in changes of texture development compared to a Cu film. The pole figure recorded in Cu{111} reflections (Figure 2a) shows relatively strong two axis <100> texture for the 50 nm thick Cu-Ag film. Simultaneously a weak <111> wire texture is observed. Comparison to Cu films (Figure 1a) shows, that Ag co-deposition with Cu enhances the texture formation in the Cu film. The <100> biaxial texture observed for 400 nm undoped Cu film (Figure 1b) appears already at 50 nm thickness in this film (Figure 2a). However, the additional <111> wire component was not observed in Cu/[100]Si films. Thin Ag films have <111> wire texture on (100)Si in our experiments. Based on these two experiments we can propose that Ag enhances both the epitaxial growth of Cu on (100)Si and the <111> wire texture in thin (50 nm) films.

Increasing the thickness to 400 nm (Figure 2b) preserves the biaxial <100> texture obtained in thin Cu_{9}Ag_{1} films (Figure 2a). No further selection processes are effective above 50 nm film thickness (Figures 2a and 2b).

Morphologically both the thin and thick Cu_{9}Ag_{1} films belong to the Zone III structure [9,10], i.e. the growth of the columnar like Cu crystallites is blocked by the overgrowing Ag crystals on the top of which repeated nucleation of Cu occurs, assuring re-nucleation of Ag as well. The result is a composite in which the grain size of both components is smaller than the thickness of the film both in lateral and in film normal directions (Figure 2c).

Only wire textures were observed in the eutectic (60 at% Ag) films, characterised also by very small grain size [4]. Both the thin (50 nm) and thick (400 nm) films have a pronounced <111> wire texture which is observed for both Cu and Ag correspondingly (Figure 3a and 3b). In the case of this composition no evidence of the breaking of the natural SiO_{x} layer was observed, i.e. Ag is reducing the activity of Cu to oxygen.

Figure 3. Cu (a) and Ag (b) <111> pole figures of Cu-Ag films of eutectic composition of 400 nm thickness and TEM dark field cross section image of the 400 nm thick film (c).

Summarising, Cu-Ag films were deposited in vacuum of 10^{-5}-10^{-6} mbar onto freshly cleaned Si wafers. The composition of the films corresponded to Cu, Cu_{9}Ag_{1}, Cu_{4}Ag_{6} and Ag in connection to the physical and morphological properties of these films [4].

At 50 nm thickness (T_s=20°C, v=1nm/s) the pure Cu films have no measurable texture. Texture formation appears when Ag is added. Sharp biaxial <100> texture (epitaxy) is observed in films of Cu_{9}Ag_{1} composition. Strong one axis <111> texture appears in the nanocomposite [4] of the eutectic composition (Cu_{4}Ag_{6}).
In films of 400 nm thickness (T_s=20°C, v=1 nm/s) <100> biaxial texture is present both in undoped Cu and at Cu/Ag composition. However, in the eutectic composition again one axis <111> texture is observed.

Both thick and thin Ag films have <111> one axis texture.

Consequently, in thin and thick films of Cu/Ag composition Ag enhances the development of biaxial <100> texture through the selection processes [1, 2] and the formation of a <111> wire texture.

In the films of eutectic composition (Cu/Ag) formation of <111> wire texture takes place. The selection processes favouring the growth of <100> Cu crystallites are suppressed due to the very small grain size in these films.

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