

Alkanethiol self-assembled monolayer on copper polycrystalline thin films: Influence on resistivity

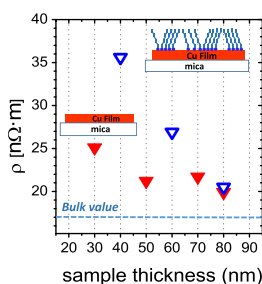
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HIGHLIGHTS

- The Dodecanethiol-SAMs formation onto Cu films is evidenced from XPS measurements.
- The Dodecanethiol-SAMs shown to be a protection film of the Cu oxidation.
- The resistivity of the Dodecanethiol-SAMs/Cu films is lower than the bare Cu films.

GRAPHICAL ABSTRACT



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ABSTRACT

Thin polycrystalline copper films of low surface roughness and low electrical resistivity were deposited by physical vapor deposition onto mica at room temperature and in thicknesses ranging from 10 to 80 nm. The crystalline orientation of the films was mainly in the [111] direction, with a surface roughness of under 8.0 nm for thicker films. The copper films were coated with dodecanethiol (DDT), $\text{CH}_3(\text{CH}_2)_{10}\text{HS}$ by direct immersion into a millimolar solution of the molecules in ethanol for 20 h. Self-Assembled monolayers (SAMs) formation was observed based on XPS studies. The results showed that DDT-SAMs were an effective barrier against the oxidation of the metallic surface, and the resistivity increased between 15% and 70% over the bulk value, depending on the film thickness.

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1. Introduction

Continuous demand for the miniaturization of electronic devices has stimulated material science researchers to focus on the properties of thin films, including their resistivity and morphology, and how these are related. Several materials were introduced in interconnect (i.e., Au and Al), but Cu appears to be the most important metal in the microelectronics industry owing to its excellent thermal and electrical conductivities [1]. However, it is an

active metal that does not resist oxidation well when exposed to air [2–5], even at room temperature. Such an oxide layer is thought to induce trap states in the interface that can reduce the thermal and electrical conductivities [3]. Prevention of copper oxidation in copper metallization technology is a major challenge for the electronics industry. Copper is mainly used in electronic packaging, interconnection wires, etc. Corrosion of copper at the interface of a Cu–Al bonding area decreases the interfacial shear strength and weakens the Cu–Al bonding [6]. An effective approach to solve this problem is surface modification using self-assembled monolayers (SAMs) [7–10]. In many cases, SAMs on active substrates such as copper are densely packed monolayer coatings [11], which can be used as a barrier for oxidation.

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SAMs are thin organic films that form spontaneously on solid surfaces. A special case of alkanethiol SAMs has been shown to be useful as passivating layers and also for the modification of surface properties. Potential applications include wetting, adhesion [12], friction, chemical and biological sensing, ultrafine scale lithography [13], and protection of metals against corrosion [14,15]. The majority of work on alkanethiol SAMs has focused on their fundamental importance in understanding interfacial properties. In the case of alkanethiols on a face-centered cubic metal (such as gold, silver, nickel, and copper), they are strongly chemisorbed on the surface by forming a covalent-like bond between metallic and sulfur atoms following the cleavage of the sulfur-hydrogen bond [16–18].

SAMs have been prepared on copper surfaces and are characterized by IR reflection, X-ray photoelectron spectroscopy (XPS), and wetting measurements. Although the Cu surfaces differed in structural details from the extensively studied Au(111) surface, it has been concluded that the structures of SAMs on copper are qualitatively similar to those on gold [17]. Laibinis et al. reported that alkanethiols adsorb from a solution onto copper surfaces and form densely packed SAMs [7,16]. The adsorbed species is a thiolate. The hydrocarbon chain is primarily extended and is oriented close to the normal to the surface. Differences in the formation of the monolayers on copper and gold reflect the difference in the reactivity of the copper surface, particularly its susceptibility to oxidation on exposure to air [18–20]. The copper surfaces oxidize rapidly during sample preparation. It has been proposed that the oxide layer on the copper surfaces may be important for the reproducible formation of high-quality monolayers [21].

Oxidation of copper surfaces [3] and alkanethiol SAMs inhibiting the oxidation [10] of copper in air have been reported in studies on thicker sheets. However, the study of the oxidation and effective protection of thin films on the nanoscale [4,9] and the influence on their properties (such as mechanical or electrical) need to be further studied.

In this work, we studied the resistivity of thin copper films covered and uncovered with alkanethiol. The thin films were deposited onto mica at room temperature and at thicknesses of up to 100 nm. The crystalline orientation of the films was determined by XRD, while surface topography was studied by AFM. Oxidation and anchoring of the molecules to the surface were studied by XPS. Finally, the resistivity of DDT-Cu and bare Cu samples were studied by the four-point method.

2. Experimental

The copper thin films were prepared under UHV conditions, starting from copper shot (Alfa Aesar 99.9999%), using an e-beam (Telemark) over freshly cleaved mica (high-quality V1, SPI). The rate of deposition was 1 nm/min. In the present study, the thickness varied from 10 to 100 nm. The sample holder did not have a cooling/heating system, and the final temperature of the substrate was 50–80 °C depending on the thickness. The thickness of the samples was checked in situ with a quartz crystal monitor located near the substrate during the evaporation and contrasted by the Tolansky method.

The composition of the films over each step was tested by XPS using an XPS-Auger PerkinElmer electron spectrometer Model PHI 1257 running under ultrahigh vacuum conditions, a hemispherical electron energy analyzer, and an X-ray source that provided unfiltered $K\alpha$ radiation from its Al anode ($h\nu = 1486.6$ eV). The pressure of the main spectrometer chamber during data acquisition was maintained at around 10^{-7} Pa during the measurements. The binding energy (BE) scale was calibrated using the peak of adventitious carbon, which was set to 284.6 eV [22]. All spectra were

recorded using grazing angle emissions. The surface morphology of the copper films was examined by XRD using Bruker D8 Advance equipment and Cu $K\alpha$ (1.5418 Å) radiation. The measurements were performed in a $\theta-2\theta$ scan mode. In the Bragg-Brentano geometry, the steps and acquisition time were 0.005 and 1 s, respectively. The topography and surface roughness were studied by atomic force microscopy (AFM) in contact mode, using SPM1 from Omicron operating in a high vacuum. An AFM tip with a force constant of 0.02–0.77 N/m and a tip radius of 10 nm was used. The topographic images were processed by using WSxM software [23].

After deposition, the copper thin films were immediately immersed for 20 h in 1 mM dodecanethiol (DDT; Sigma Aldrich, 99.99%) solution in absolute ethanol (Norma Pur, an analytical reagent). Then, the samples were rinsed with absolute ethanol and dried under a N_2 stream [24]. The DDT-Cu samples were characterized by AFM and XPS. In addition, resistivity measurements were performed by the four-point method [25] for the bare Cu and DDT-Cu samples.

3. Results and discussion

The texture of the Cu films is shown in Fig. 1(a), which indicates the XRD patterns for samples with different thicknesses. In order to correctly identify the peaks diffracted from the deposited films, the substrate of the mica was also investigated. In the figure, this is indicated by a blue triangle. The film growth was mainly oriented in the [111] direction, $2\theta = 43^\circ$ [26]. The crystalline nature enhanced with thickness. No other crystalline orientations were observed. The FCC crystal structure of Cu minimizes its surface energy on this face. The same orientation was observed for thin films evaporated on glass [27] or silicon [28].

The crystallite size was calculated using the Scherrer formula. Here, the FWHM of the [111] peak was estimated by adjusting a pseudo-Voigt curve [29]. Under a nominal thickness of 10 nm, no crystalline orientation was observed, probably because the crystallite size conforming the films is under the resolution of the equipment. The crystallite size dependence on the thickness is shown in Fig. 1(b). The relation is linear and has the same value up to 50 nm of thickness. At higher values, the crystallite size becomes lower than the thickness, or linear behavior with the thickness is observed but with a lower slope value, as indicated by the eye guide lines. This means that the grain constituting the films is columnar up to a thickness of 50 nm.

The topography of the surface was imaged by AFM, as shown in Fig. 2. A representative image in 2D is shown for thicknesses of (a) 10 nm and (b) 50 nm for uncovered copper films. The thinner film is constituted by a distribution of grains of less than 50 nm diameter. For the thickest films, a distribution of grains different from that of circular grains is observed. This behavior can be attributed to size evolution and/or coalescence of the grains. These images are in agreement with the Volmer-Weber growth mode obtained using metal onto insulator surfaces. In both cases, a fully covered substrate with a homogenous grain distribution is clearly observed. The grain size is typically more than the nominal thickness [30].

The influence of the film thicknesses on the morphology was investigated by calculating the surface roughness over 500×500 nm² areas for each thickness. The result is displayed in Fig. 2(c). For thin-film deposition methodologies in which the film thickness t is proportional to the time of deposition, in asymptotic limits, the power law relation for surface roughness σ is $\sigma \propto t^\beta$ [31]. From our data, the power exponent is $\beta = 0.75$, which agrees with the computational simulation of the FCC metal growth [32]. This anomalous scaling exponent is attributed by some authors to nonlocal effects such as shadowing instabilities and bulk diffusion during the growth of the copper film [33]. In our case, even if the

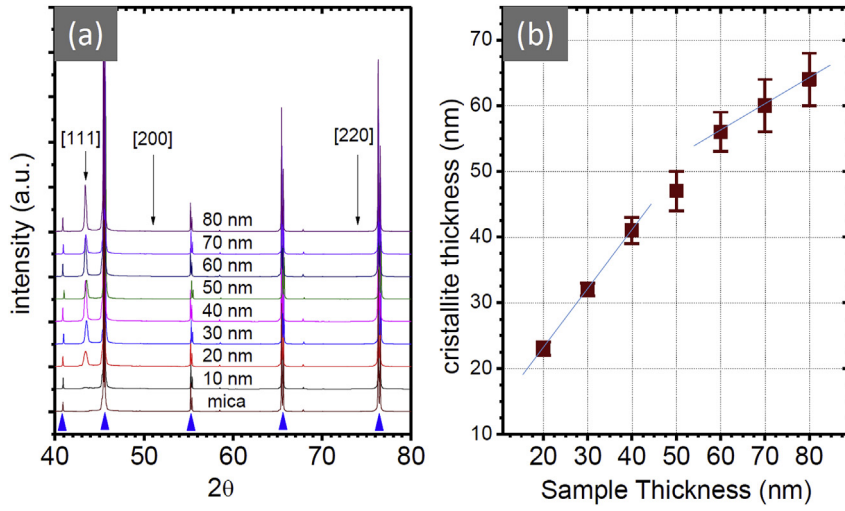


Fig. 1. (a) XRD pattern of Cu films with different thicknesses and mica substrate. Film growth is in the [111] direction. (b) Crystallite size dependence on sample thickness from the FWHM of the [111] peak.

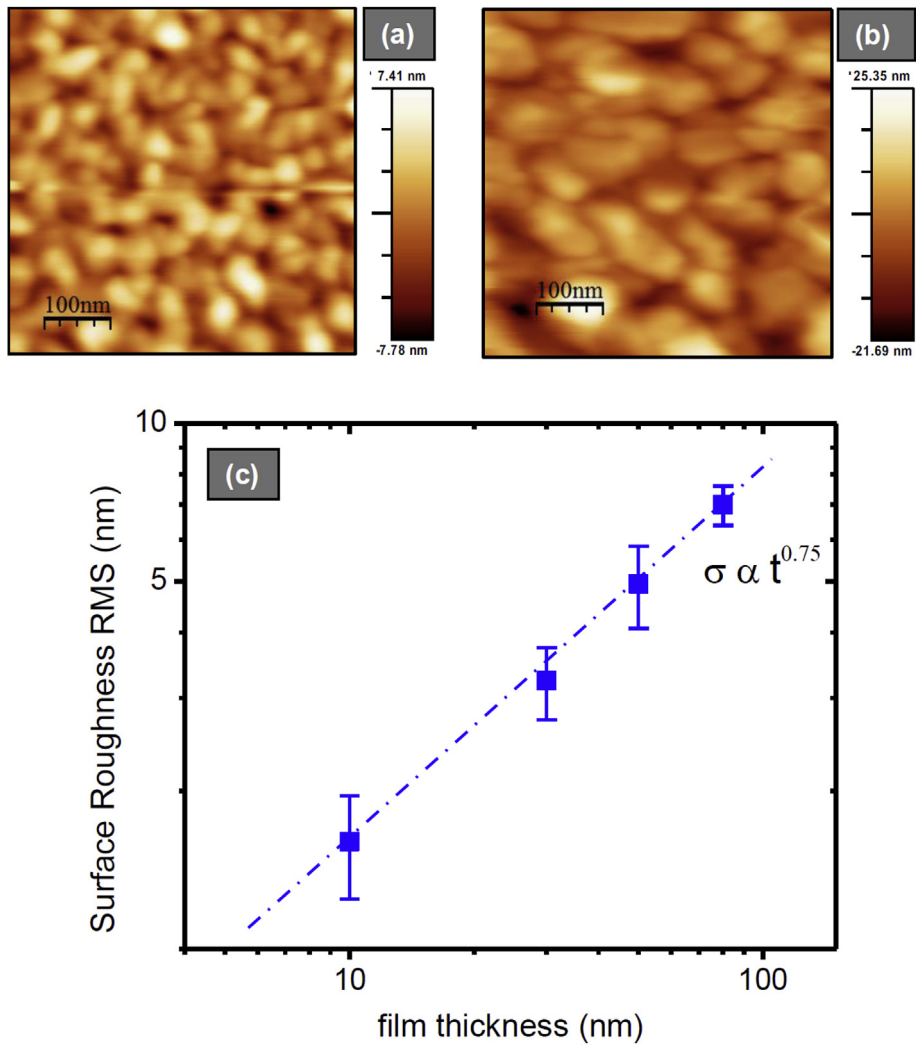


Fig. 2. Topographic image of (a) 10-nm- and (b) 50-nm-thick Cu films. Grains are observed. (c) Dependence of surface roughness on thickness.

sample is not rotating, the e-gun ejects the material normal to the substrate surface. In this case, shadowing instabilities are not expected but are not excluded either. In contrast, the sample temperature is relatively low: close to 350 K for the thickest film. At this temperature, the bulk diffusion makes a very minor contribution. For a better discussion of surface roughness, we need to investigate this topic further.

The surface composition of the film was studied by XPS. The spectra were acquired via grazing angle emission to study the topmost surface of the films. The results were independent of the copper thickness. Therefore, the analysis presented here corresponds to a sample of Cu of thickness 80 nm only. The survey spectra are shown in Fig. 3(a) for the fresh copper film and the uncovered and DDT covered films. The fresh copper films correspond to a sample deposited and immediately transferred to the XPS chamber without breaking the vacuum. This sample is free of contamination (oxygen and carbon); the small intensity of C 1s and O 1s can be attributed to the X-ray source. In order to make an accurate comparison between the uncovered and DDT covered films, the oxidation of the films was investigated by exposing them to air for 24 h. Both cases show oxidation, as evident from the appearance of an oxygen peak, but it is much higher in the case of the nude copper. In addition, some signal of the carbon is observed. For the uncovered surface, the carbon signal can be attributed to

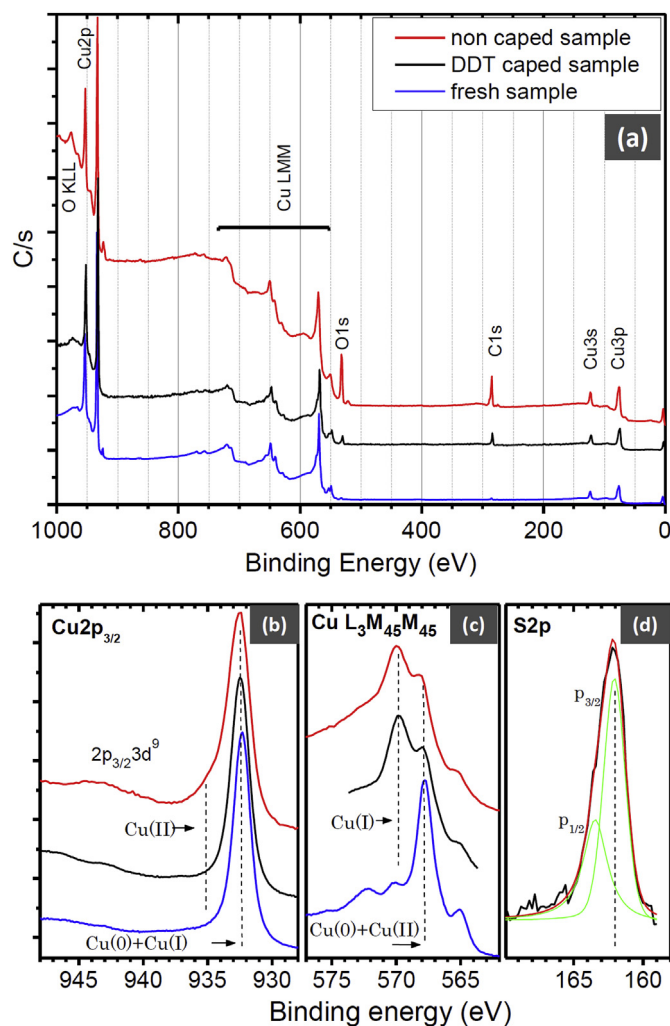


Fig. 3. (a) XPS spectra of samples at full range. High-resolution XPS spectra of (b) Cu 2p, (c) Cu Auger, and (d) S 2p signals.

contamination absorption from the air [2]; for the DDT-Cu samples, this signal arises from the carbon in the alkane chain [10].

A high-resolution study of the signal from (b) Cu2p, (c) Cu(LMM), and (d) S2p is also included in Fig. 3. For the fresh copper films (blue line), the Cu2p signal is fitted with a single peak at a binding energy of 932.8 eV and FWHM of 1.45 eV. This peak is attributed to Cu(0) and Cu₂O. The Auger signal Cu(LMM) exhibits two main peaks at a binding energy of 567.8 eV, corresponding to a metallic state and CuO at the surface [2,3,7,34]. The second principal peak at 569.8 eV corresponds to Cu₂O [3,20,34,35]. The copper films exposed to atmospheric conditions for 24 h (red line) show a dramatic change in the appearance of “shaken up” satellite peaks in the Cu2p signal at 944.0 eV [2], showing the formation of a thick oxidized layer on the top of the surface. In addition, at the metallic peak, a shoulder is observed. This is attributed to CuO with a binding energy of 934.0 eV and FWHM of 1.75 eV. The same feature is observed for the DDT-Cu (black line), but the peaks are less intense than those of the bare Cu films. The Cu(LMM) Auger signals for samples with and without DDT show the same features; the most intense peak now corresponds to Cu₂O. This is consistent with the formation of Cu₂O/(CuO+Cu) on the surface, as reported by Laibinis and Withesides [6]. From the Platzman equation for the determination of the oxide film [2,3], Cu₂O, and/or CuO, we estimated a thickness of 0.8 nm for DDT/Cu and 1.5 nm for bare Cu film after 24 h of exposure to air.

Anchoring of the DDT molecules on the surface is evidenced by a sulfur signal apparition with a double peak contribution at binding energies of 162.0 eV (2p_{3/2}) and 163.2 eV (2p_{1/2}) [10,20]. This indicates that the molecules are mainly anchored to the surface trough of the sulfur atom and not to thiolate or sulfonate cluster. A similar observation is noted for SAMs on a metallic surface [7,17,35].

Fig. 4 shows the relationship between the electrical resistivity and the film thickness for bare Cu and DDT-Cu films after the samples were exposed to air for 24 h. The thinnest film measured was 30 nm. At lower values, the copper films without DDT-SAMs became electrically discontinuous after 24 h in atmospheric conditions.

Resistivity $\rho(T)$ was studied from 4.2 to 100 K. The resistivity became higher with increasing film thickness, but the curves were not organized by the film thickness. In fact, 70-nm-thick films showed higher resistivity than 50-nm-thick films. This phenomena can be explained by the change in the crystallite size at over 50 nm of thickness, and the formation of a pseudo-second layer of copper films, thus increasing the resistivity [36]. It is expected that another charge transport scattering mechanism can be derived from the $\rho(T)$ slope of thickness 70 nm, which is quite different from that obtained using other thickness values. In addition, the resistivity values of the non-covered copper films are higher than those of DDT-SAMs/Cu. This difference is stronger for thicker films.

Non-protected Cu films have the highest value of resistivity, 34,6 nOm, for a 40-nm-thick film. The resistivity decreases with increasing film thickness up to 80 nm. The electrical resistivity is comparable to that of the Cu film prepared by a cathodic vacuum arc method [37] and is lower than that for the Cu film prepared by the magnetron sputtering method [28,38]. The dependence of resistivity on the film thickness is inversely dependent on the surface roughness and crystallite size. In contrast, the mean free path (MFP) was calculated using the Drude theory for the DDT-SAMs/Cu films at 4.2 K. The MFP over the thickness is ordered by thickness, and the mean free path is a few times higher than the thickness.

Variations in the electrical resistivity are directly related to the topography and morphology of the films. The DDT-Cu samples show lower values of resistivity over the non-capped Cu films owing to oxidation protection. This has two effects: it keeps the surface roughness almost constant, as observed with the as-

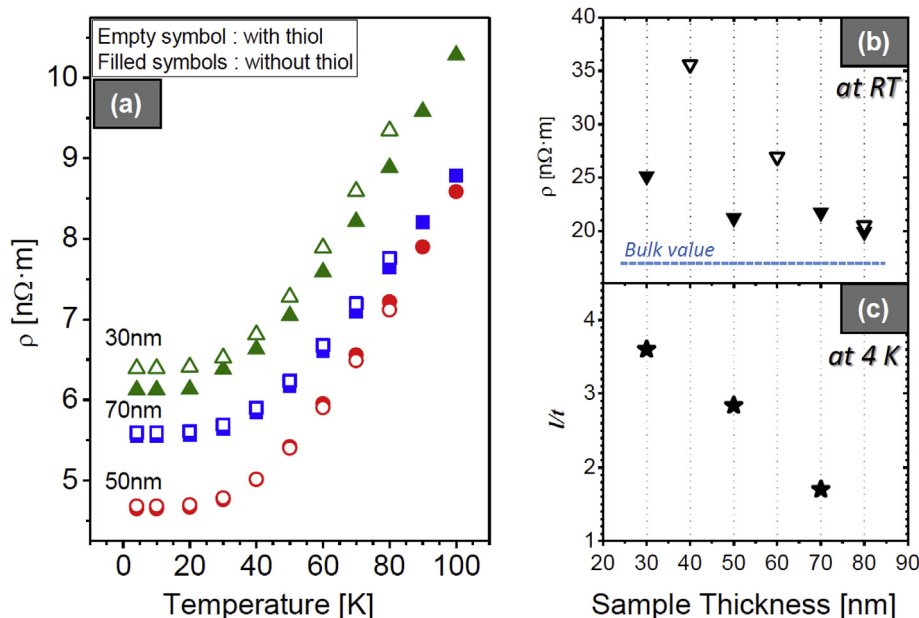


Fig. 4. (a) Resistivity of samples as a function of temperature for copper capped with DDT (empty symbol) and bare (filled symbol). (b) Resistivity of samples as a function of nominal thickness at room temperature. (c) Ratio between the mean free path and thickness as a function of nominal thickness.

deposited sample, without changing the grain size; and/or it avoids the formation of oxide films on the top, thus decreasing the nominal thickness. In order to obtain a conclusive observation, further studies must be performed.

The DDT coverage of the copper surface is shown to be a barrier to oxidation. Deterioration of the thin films is inhibited by using these nanometer-thick film coverages. In fact, the resistivity of the DDT-Cu is lower than 70% with respect to that for bare Cu for the thicker film, measured after 24 h of air exposure.

The stability of the DDT-Cu thin films can be applied to the electronics industry, for example, in electronic packaging solutions, or to increase the life of interconnection wires and avoid cracking owing to copper oxidation.

4. Conclusion

Thin polycrystalline Cu films were deposited by e-beam to up to 100 nm of thickness, and were capped by DDT-SAMs. The Cu films were [111] oriented with a surface roughness of under 8.0 nm. Oxidation in air conditions was reduced by the DDT coating, as compared to that of bare Cu films. This means that the DDT-SAMs were an effective barrier against oxidation of the metallic surface. The electrical resistivity increased to up to 15% and 70%, depending on the bulk value depending on the thickness, but the resistivity of the DDT-SAMs/Cu films was lower than that of the oxidized Cu films.

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