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Recovery of electrical resistance in copper films on polyethylene terephthalate subjected to a tensile strain

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ABSTRACT

Substantial recovery (decrease) of electrical resistance during and after unloading is demonstrated for copper films on polyethylene terephthalate substrates subjected to a tensile strain with different peak values. Particularly, the films strained to 5% exhibit full resistance recovery after unloading despite clearly visible plastic deformation of the film. The recovery of electrical resistance in connection with the mechanical behavior of film/substrate couple is discussed with the help of in situ scanning electron microscopy and X-ray diffraction analysis.

1. Introduction

Fabrication of electronic devices on polymer substrates is an emerging technology which has a great potential for the production of large-area, light weight, and mechanically flexible electronics with a low cost. Although the working prototypes of full-color flexible displays [1,2], solar cells [3], and biomedical sensors [4] demonstrated that the stability and mechanical reliability of such devices are still a challenge. Fabrication, for example, of a flexible display involves integration of materials with different mechanical properties, from hard and brittle barrier layers and transparent conductors such as indium tin oxide, over ductile metal contacts and conductive interconnects to elastic polymer substrates. The understanding of the mechanical and fracture properties of such composite structures is crucial for bringing the technology to mass production. If electrical connection between different elements of a flexible electronic device is to be served by copper metallization, the electrical stability of copper layers bonded to polymer substrates is required.

The growth of electrical resistance of thin metal films on polymer substrates was investigated by several groups for Cu on polyimide [5–9], Al on polyimide [10,11], Al on polyethylene terephthalate (PET) [12] and Ag on PET [13]. However, the behavior of electrical resistance during and after unloading remains virtually unexplored. Moreover, scanning electron microscopy (SEM) micrographs of *unloaded* samples are often used to connect the mechanical phenomena (e.g. localized thinning, cracking, delamination) with the evolution of the resistance during *loading* which is valid only under the assumption that the relaxation processes during unloading are negligible.

In this study the behavior of electrical resistance of ultra fine grain Cu films on PET is analyzed during the entire tensile experiments (loading and unloading) as well as 24 h after it. Significant reduction of the electrical resistance observed during and after unloading supports the importance of relaxation processes for the full understanding of the behavior of Cu/PET composite systems. The recovery of electrical resistance is discussed with the help of in situ SEM analysis as well as with in situ X-ray diffraction (XRD) stress measurements of the Cu film.

2. Experimental details

Cu films with a thickness of 200 nm were DC magnetron sputter deposited on a commercially available, biaxially oriented 23 μm thick Hostaphan® RN PET substrate. Before the deposition of Cu film, a 5 nm Cr adhesion layer was applied, also via DC magnetron sputtering, to improve the adhesion between the Cu film and the PET substrate. The copper films have the grain sizes distributed in the range of 70–190 nm. The test samples have the width of 5 mm and the gauge length of 20 mm was used in all tests. The tensile straining experiments were performed on an MTS Tytron 250® Universal testing machine with a constant strain rate of 0.0001 s^{-1} for loading and unloading. Altogether 30 samples were subjected to three different values of maximum strain

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(10 samples in each set): 5%, 10%, and 20%. After loading, the samples were unloaded to the strain of 0% for peak strain of 5%, 2% for the peak strain of 10% and 10% for the peak strain of 20%. Then each sample was kept in an unloaded state for 24 h in order to extract the residual plastic strain and final resistance. The 4-point-probe in situ resistance measurements were performed by a Keithley 2000 multimeter with the probing contacts incorporated into the grips of the straining instrument. The resistance of the film under the grips which remains constant during straining was subtracted from the total resistance measured by the ohmmeter. Further detailed information on the in situ 4-point-probe experiments can be found in Ref. [14].

An increase of electrical resistance of a polymer-supported metal film during tensile straining can be represented as the sum of two contributions: geometric and structural. An increase of the distance between contacts and the simultaneous shrinkage of the sample in the transverse direction (Poisson's contraction) constitute the geometric contribution. An assumption that the resistivity and the total volume of a thin film remain constant (i.e. assuming a perfect plastic deformation) gives the following formula to estimate the geometric contribution to the resistance growth:

$$\frac{R}{R_0} = \left(\frac{L}{L_0}\right)^2. \quad (1)$$

In Eq. (1), R is the measured resistance, R_0 is the original resistance, L is the gauge length of the sample, and L_0 is the original gauge length [6]. The structural contributions include the change in point defect density, grain boundary density, cracking, necking (i.e. localized thinning) as well as the formation of dislocation pile-ups or intrusions. Note that theoretically the point defect and grain boundary density can decrease when the film is strained which, in turn, may lead to a decrease of resistance.

In order to correlate the changes in electrical resistance to the deformation occurring in the Cu film, tensile straining of the film-substrate systems was performed in situ inside a scanning electron microscope (SEM, LEO 1525) using a small scale tensile device from Kammrath and Weiss (Dortmund, Germany). Each in situ experiment was carried out using the same strain rate as the 4-point-probe experiments ($0.0001\ s^{-1}$). Inside the SEM, micrographs were made at every straining step, approximately every 200 μm of displacement to a maximum strain of 20% as well as during the unloading of the strain to a load of zero (approximately 13% strain). Additionally, the stress in the Cu film was measured with in situ X-ray diffraction (XRD) at the BESSY II synchrotron source using end station KMC-2 and the $\sin^2\psi$ method [15]. The setup was in the reflection geometry using a beam wavelength of 0.17714 nm. The (111) Cu peak was measured at four different psi (ψ) angles using a detector exposure time of 5 s during the entire loading and unloading of the sample. In the case of the in situ XRD experiments, an Anton Paar TS600® straining stage was utilized using a continuous loading function (no stopping) and a strain rate of $0.00001\ s^{-1}$. The stresses in the Cu films obtained by the X-rays were registered simultaneously to the stresses of the complete material system obtained by the load cell. Using slower strain rate allowed for more X-ray data to be collected and also has no effect on the resulting deformation or fracture behavior of the Cu film [16]. All 4-point-probe and XRD experiments were performed at room temperature and in air.

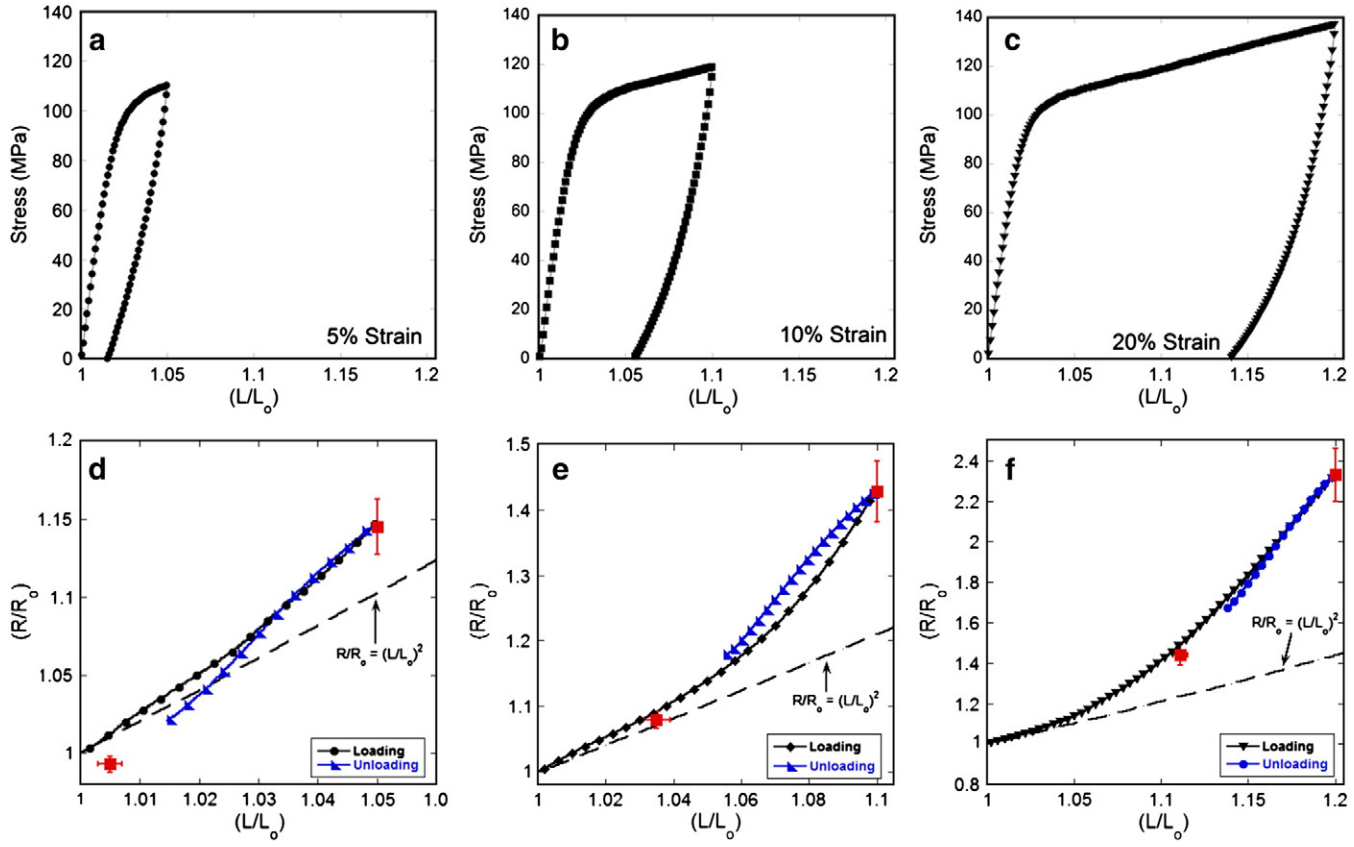

Fig. 1. Combined film and substrate stress (a–c) and the relative resistance (d–f) vs. relative elongation for 5%, 10%, and 20% strain. The loading and unloading parts of resistance curves (d–f) are shown by black and blue symbols, respectively. The single red square symbols in (d–f) indicate the average relative resistance at maximum strain and the final relative resistances and elongations measured after 24 h.