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

O. Glushko [a,*], V.M. Marx [a,b], C. Kirchlechner [a,b], I. Zizak [c], M.J. Cordill [a,d]

[a] Department Materials Physics, Montanuniversität Leoben, Jahnstrasse 12, 8700 Leoben, Austria
[b] Max-Plank-Institut für Eisenforschung GmbH, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany
[c] Helmholtz-Zentrum Berlin for Materials and Energy, Albert-Einstein-Str. 15, D-12489 Berlin, Germany
[d] Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Jahnstrasse 12, 8700 Leoben, Austria

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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

* Corresponding author.

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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.

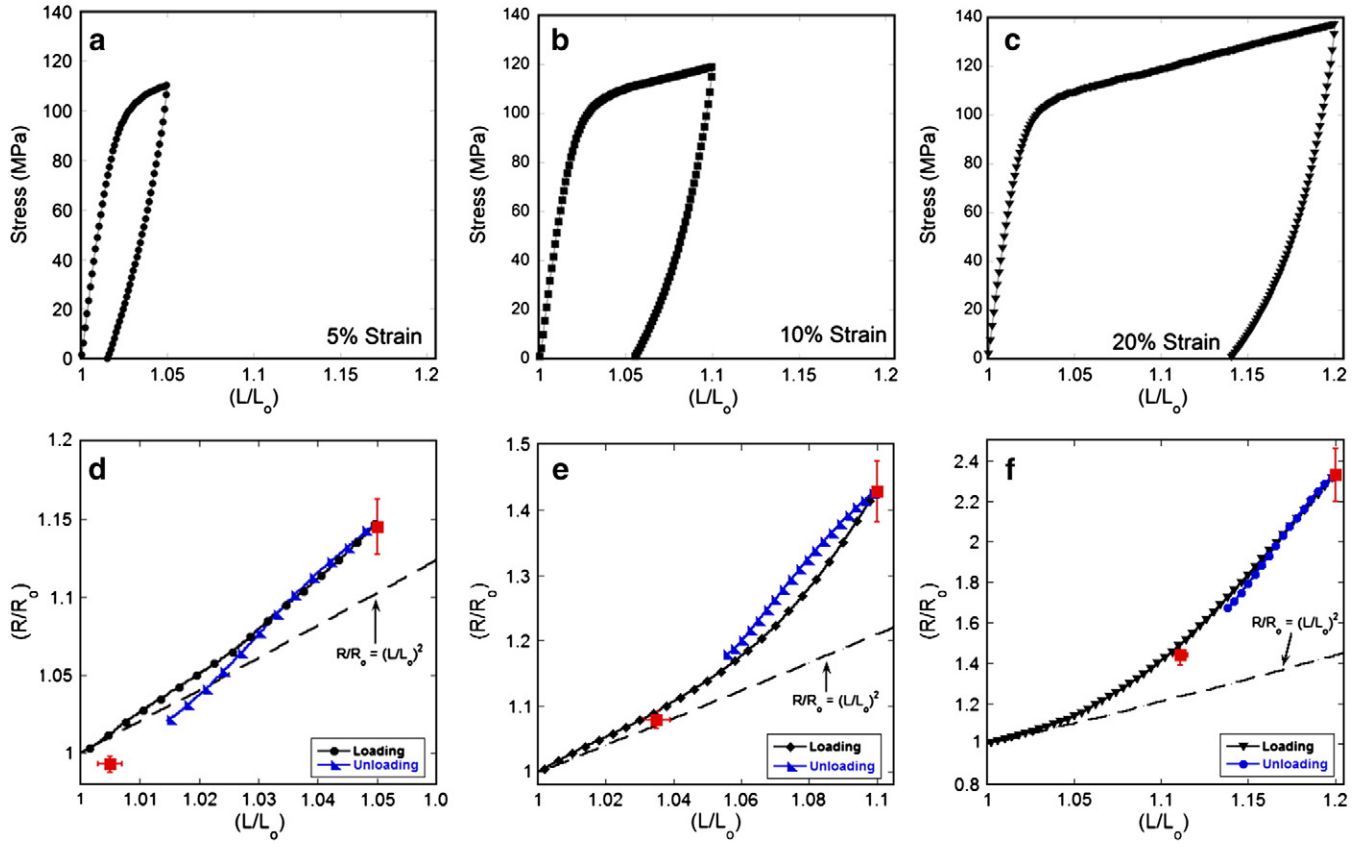

Fig. 1. Combined film and substrate stress (a–c) and the relative resistance (d–f) vs. relative elongation for 5%, 10%, and 20% strain. The loading and unloading parts of resistance curves (d–f) are shown by black and blue symbols, respectively. The single red square symbols in (d–f) indicate the average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

Table 1
Relative resistances and residual plastic strains for the examined values of peak strain.

Max strain	R/R_0 @ max strain	R/R_0 after 24 h relaxation	Plastic strain after 24 h relaxation
5%	1.15 ± 0.02	0.993 ± 0.005	(0.5 ± 0.2)%
10%	1.43 ± 0.05	1.08 ± 0.01	(3.5 ± 0.4)%
20%	2.33 ± 0.13	1.44 ± 0.05	(11.1 ± 0.4)%

3. Results and discussion

The results of tensile testing with in situ resistance measurements for the maximum strains of 5% and 20% are shown in Fig. 1. In Fig. 1a–c, the combined stress of the film and substrate (calculated as external load divided by total cross-section) as a function of the relative elongation ($L / L_0 = 1 + \varepsilon$ where ε is the strain) is shown. The corresponding relative resistance curves for Fig. 1a–c are shown in Fig. 1d–f with the dotted line describing the analytical formula for the constant volume approximation of Eq. (1). What can be observed is that the growth of resistance of the strained films follows the analytical constant volume approximation up to approximately 2% strain, increasing dramatically after this point. The faster growth in resistance can be attributed to the lack of ductility due to the small grain size. In comparison to the results of strained Cu films on polyimide, the growth of resistance in Fig. 1 is faster than reported in [6,7,9] but slower than in [8]. It is necessary to note that the grain size of the Cu films in [8] was below 50 nm and the films demonstrated rather brittle fracture.

During unloading a decrease of resistance is observed. The unloading curves in Fig. 1d–f (blue symbols) are terminated at strains where external load has reached zero. However, further decrease of the resistance was observed in unloaded samples due to viscoelastic relaxation of the PET substrate. In order to fully account for the recovery processes in a film/substrate couple after unloading, samples were left mounted in the grips for 24 h after the experiment to continuously measure the resistance. The final permanent elongation and the final resistance recorded after 24 h are shown in Fig. 1d–f by single red square data points. The average values of relative resistance at the maximum strain and after relaxation as well as the average values of residual plastic strain are summarized in Table 1. There is a significant difference between the resistances at maximum strain and after 24 h relaxation. Thus, in order to perform a correct coupled electro-mechanical analysis only the resistance after relaxation should be taken for comparison with post-mortem SEM micrographs (Fig. 2). This issue was often overlooked by other groups and the growth of resistance during loading was explained by considering the post-mortem SEM micrographs of unloaded samples.

As follows from Table 1, the final resistance of the films strained to 5% is lower than the resistance before straining. This is a surprising result especially taking into account that the surface of the film clearly exhibits visible plastic deformation (Fig. 2a) characterized by locally thinned areas as well as microcracks (indicated by the arrows). The reduction of resistance can be attributed to strain-induced reduction of point defect density or to strain-induced grain growth [7]. However, more systematic investigations are required to explain this effect.

The samples strained to 10% undergo plastic deformation as revealed by the extensive localized thinning (necks) and through thickness cracks found on the Cu film surface (Fig. 2b). Nevertheless, the mean value of the final relative resistance is lying very close to the constant volume approximation curve. This means that the growth of the resistance is mainly due to the change of the sample geometry and the effect of the residual cracks and necks on the resistance is small.

The maximum strain of 20% results in extensive cracking of the Cu film (Fig. 2c). The difference between the measured final resistance and constant volume approximation for the same residual strain is attributed to the presence of cracks in the Cu film.

The recovery of electrical resistance of copper film is attributed to the viscoelastic relaxation of the PET substrate. PET is a viscoelastic material at room temperatures [17,18] which explains the recovery of residual strain during 24 h after the tensile test shown in Fig. 1d–f. The fact that the slope of the resistance curve during unloading is nearly the same as the slope of the corresponding loading segment reveals that both geometrical (change of sample length) and structural (cracking) contributions of the resistance growth are reversible. In other words, the resistance recovery occurs due to the substrate shrinkage and closure of the cracks in the film. Moreover, since the elastic strain of PET is much higher than the elastic strain of copper film, a compressive stress arises in the film during unloading as measured with the in situ XRD straining. The stress in the copper film is shown in Fig. 3 together with external load applied to the film–substrate system. The film stress reaches a peak value at approximately 1% strain then slowly decreases with increasing strain due to plastic deformation and crack formation. During unloading the film stress goes from tensile to compressive and at a load of zero the final stress is a compressive −400 MPa. After removal from the apparatus the sample macroscopically curls into a cylinder so that the Cu film is facing outward demonstrating that a compressive stress is stored in the film due to the plastic deformation of the Cu film. This compressive stress aids in closing cracks and further decreasing the electrical resistance. Direct experimental observation of cracks closure is presented in Fig. 4 showing the surface of a Cu film recorded during in

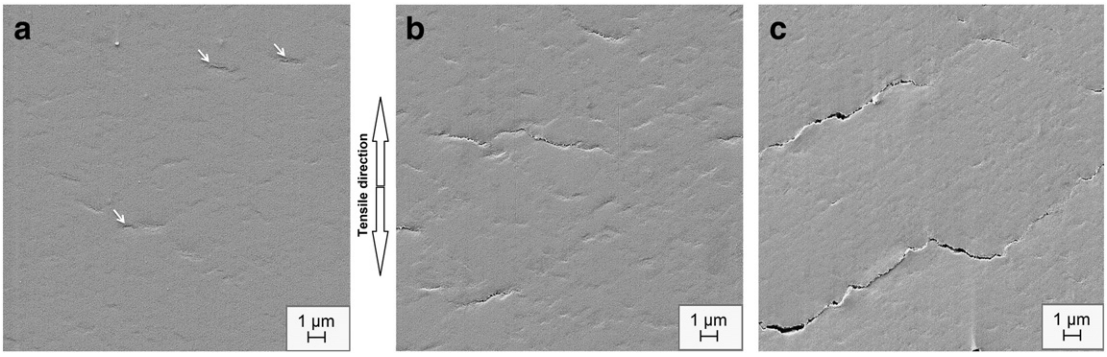

Fig. 2. Typical SEM micrographs of the Cu film after a tensile straining with the peak strain of 5% (a), 10% (b), and 20% (c). The arrows in (a) indicate the microcracks.

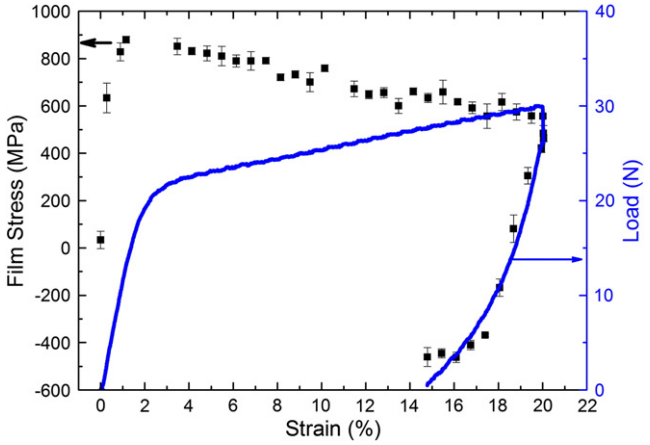

Fig. 3. In situ measured stress in the Cu film (squares, left Y-axis) and external load applied to film/substrate system (solid line, right Y-axis) as a function of strain.

situ tensile straining inside the SEM. It is clearly seen that during unloading (Fig. 4b) the crack density decreases and the surface of fully unloaded sample (corresponds to 13% residual plastic strain in Fig. 4b) exhibits similar cracking pattern as at 13% strain during loading. The linear crack density is decreased from 0.031 μm^{-1} at maximum strain to 0.015 μm^{-1} in fully unloaded state.

Using the experimental data shown above the resistance recovery behavior could be explained as follows. During unloading the resistance decreases due to the decrease of the gauge length which can be described by the formula (1) as well as due to crack closure which was observed directly (Fig. 4). Additionally, the compressive stress measured in the film (Fig. 3) acts as a driving force for further crack closure after unloading which is, together with further sample shrinkage, responsible for the resistance recovery during 24 h after the test. The resistance of the films strained to 5% after recovery is slightly lower than initial resistance. This suggests that additional changes in microstructure or point defect density might contribute to resistance recovery. It is believed that strain-assisted grain coarsening can be responsible for this resistance decrease. Strain assisted grain coarsening was observed in copper films on polyimide under similar loading conditions [7].

For the quantification of the resistance recovery process the time-dependence of the resistance of a fully unloaded samples was analyzed. Experimental resistance measured starting from the time when the external load has reached zero is shown by the open circles in Fig. 5. The simplest exponential function which adequately fits the experimental curve is shown by the dashed line and contains two terms:

$$y(t) = y_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}. \quad (2)$$

As follows from Eq. (2) the relaxation of resistance can be presented as a sum of two processes with characteristic relaxation times τ_1 and τ_2.

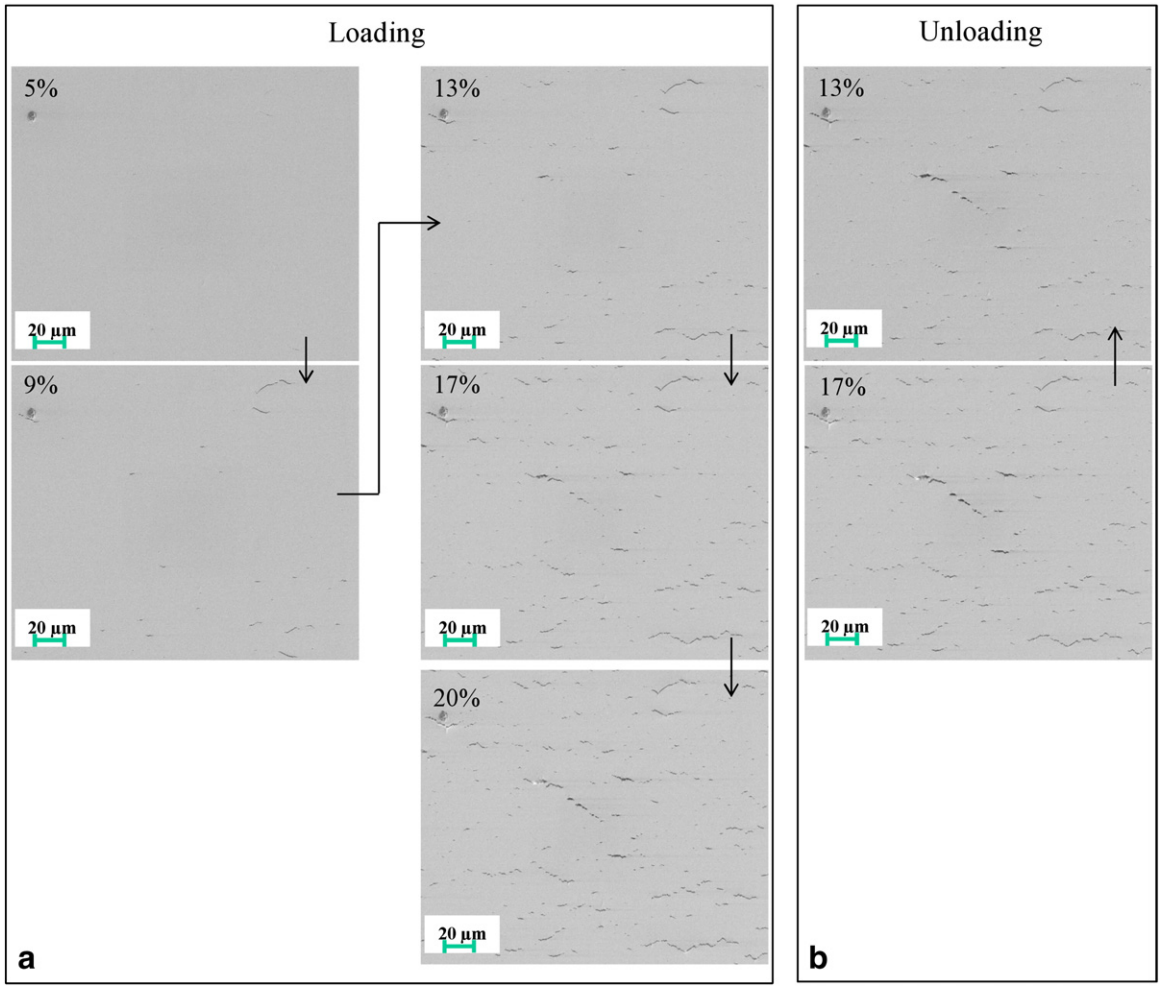

Fig. 4. SEM micrographs of the same area of the surface of Cu film taken in situ during loading (a) and unloading (b) stages of a tensile test. The straining direction is vertical. Corresponding values of global strain are shown in the top left corner of each micrograph.

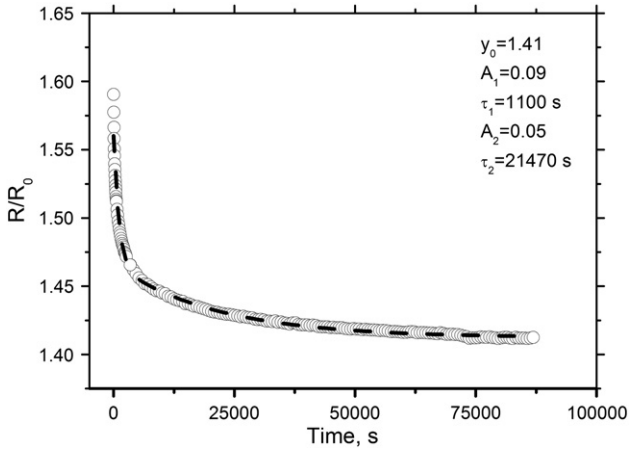

Fig. 5. Relaxation of resistance in an unloaded sample measured for 24 h. Open circles show the experimentally recorded data. Dashed line is a fit according to Eq. (2) with the parameters given on the plot.

One relaxation time (τ_1) describes initial fast decay and τ_2 describes subsequent slow decay. The typical relaxation times do not change much for different peak strains and lie in the ranges of 10–20 min for τ_1 and 5–10 h for τ_2. These relaxation times cannot be directly linked to viscoelastic relaxation or retardation times of PET because the experiments were not performed using a stepwise strain or load. Nevertheless, the recovery of electric resistance occurs at the same time scale as viscoelastic strain recovery of PET in creep-relaxation experiments [17,19]. The values of τ_1 indicate that the resistance should be recorded for at least 1 h after the experiment in order to obtain the correct value of the final resistance of a film.

4. Conclusions

It has been demonstrated that viscoelastic relaxation of the PET substrate results in significant recovery of the resistance of the copper film during unloading as well as during the next 24 h in fully unloaded samples. Resistance recovery occurs due to both geometrical shrinkage of the sample and closure of the cracks. For a maximum strain of 5% the resistance of the film after straining is lower than originally measured. This decrease in resistance could be caused by strain-assisted grain growth or other defect reducing processes leading to reduced electron scattering. By analyzing the time-dependent relaxation of resistance in fully unloaded samples it is shown that initial exponential decay of resistance has characteristic relaxation times in the range of 10–20 min independent of the maximum applied strain. Thus, in order to properly characterize and compare the electromechanical behavior of metal films on polymers for flexible electronic applications, the behavior not only at a maximum stress or strain should be examined, but also during unloading and at least 1 h afterward.

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