Cryo-FIB-Preparation and Cryo-SEM Investigation of Gold Nanolayers Used as Absorber for Laser Welding of Polymer Foils

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Summary: The morphology of welded polymer foils was investigated by Scanning Electron Microscopy (SEM) using Focused Ion Beam (FIB) technology for cross-sectional preparation. Due to the sensitive structure of the copolymer Ethylene Tetrafluororethylene (ETFE), FIB preparation and SEM investigation were performed at cryo conditions. A gold nanolayer was used as absorber for the laser beam to weld the transparent copolymer foils. The embedding of the gold nanolayer inside the welding seam and its influence on the mechanical stability of the welding seams was demonstrated.

Keywords: cryo preparation; electron microscopy; ethylene tetrafluoroethylene copolymer; laser welding; nanoparticles

Introduction

Laser Welding of polymer components and foils is an important technology in polymer processing. If polymer have to be joined which are transparent for the laser light, an additional absorber materials have to be placed between the joining partners. Due to the absorbed Laser energy, the polymer melts locally and both components will be joined. Usually, organic dyes, e.g. based on perylenes, act as absorber material. By various chemical modifications, the optical properties of the dyes are adjusted with respect to the Laser wavelength to get optimal absorption of the Laser light. During thermal heating, the dyes are chemically modified and change their optical absorption. Therefore, the welded seam becomes optical transparent. The dyes which are introduced into the welded polymer seam generates unwanted chemical modifications of the polymers. Hence, other materials of other physical effects for light absorption have to be found for incorporation energy into the interface between the joining welding partners.

Due to their plasmon resonance, thin noble metal films and noble metal nanoparticles exhibit an optical absorption in the visible part of he optical spectrum.[1] The spectral position, intensity and half width depend on the nanostructure of the thin film as well as on size and shape of the nanoparticles. Anymore, Plasmon resonance is influenced by the surrounding medium. The Laser light which is absorbed by the plasmon resonance, will be transferred by photon phonon coupling to oscillations of the nanoparticle metal lattice. The produced heat is transferred to surrounding polymer media. The polymer melts locally, which results in a mechanical sufficient joining of the polymer foils and components.[2] Otherwise, the increasing of the temperature induces diffusion processes of metal atoms,[3,4] and at much higher energies, also evaporation of the metal atoms. Therefore, the size and shape of the nanoparticles change and the optical properties of the welding seam too. But, if nanoparticle or thin metal films are embedded in the welding seam, it is necessary to investigate their morphology

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inside the welding seam. Especially, it is substantial to find out, how the metal particles and thin films disturb the polymer morphology in the joined region. Therefore, expensive microstructural investigations with electron microscopy, especially of cross sections are necessary.

Usually, sample cross sections are made by the well-established microtomy or cryo-microtomy.[5] Otherwise, Focused Ion Beam (FIB) technology can be used to prepare cross sections of polymer samples on predefined positions. Although the FIB technology is widely used in the semiconductor industry, the preparation of polymer solid interfaces is still at the beginning.[6,7] Resulting from the previously limited availability of the FIB technology, only a few studies about FIB preparation are known. In polymer material science FIB preparations are used for nanostructuring polymeric surfaces[8,9,10,11] as well as to investigate aging effects of polymer components.[12] The use of FIB in polymer sample preparation is delicate, because it can induce amorphization of the sample surface, scission and/or cross linking of polymer chains, shrinkage of the chains, and modification of the surface chemistry. To suppress such damaging effects of the ion beam on polymers, special preparation parameters has to be used.[13,14] Otherwise, FIB prepararion at low temperatures down to liquid nitrogen temperature (Cryo-FIB) is an option to reduce thermal input of the gallium ion beam and modification during FIB preparation.

Experimental Part

Materials

Because of their application relevance, welding seams made by laser welding of transparent foils made from the copolymer Ethylene Tetrafluoroethylene (ETFE) were selected. Before laser welding, one of both welding partners was coated with a thin gold film made by magnetron sputtering. The laser welding was performed with a continuous semiconductor diode laser (50 W) at a wavelength of 808 nm together with the globo welding system distributed by Leister. The laser beam was spread to a diameter of about 3mm. Both welding partners were put together with the gold nanolayer between them. During welding, the mechanical load can be adjusted between 80 N and 100 N.

The optical properties of the sputtered gold film on ETFE foils were measured in the spectral region between 400 nm and 1000 nm with a microscope spectrometer (J&M TIDAS spectromecter on Carl Zeiss Axioplan 2). Light microscopy was performed in transmission mode with an Olympus BX 51 microscope.

FIB Preparation and SEM Investigation

Because of its high resolutions, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are well-suited to observe the nanostructure of embedded metal nanoparticles and thin films. Otherwise, the special assembly of the welding seams requires an effective cross-sectional preparation. Usually, cross-sections will be generated by ultramicrotomy or cryo ultramicrotomy. This cross-sectional preparation and the following SEM investigations of ETFE welding seams will be described elsewhere.[15] Alternatively to microtomy, focused ion beam (FIB) technology offers a new possibility for cross-sectional preparation on preselected sample positions.

In a focused ion beam (FIB) work station, a focused gallium ion beam is used for ablation and deposition of materials on the sample's surface.[16] The resolution of the focused ion beam on the sample is below 10 nm. Using these ion beams, the cross-section of a sample can be prepared. The secondary ions and electrons from the ion beam are also used for surface imaging, but nowadays the focused ion beam source is incorporated into a high-resolution scanning electron microscope (dual beam technology). The potential of this technique ranges from top-down structuring (etching or deposition of nanostructures) up to 3D tomographic characterization in complex microstructures and composite materials.[17,18] Furthermore, the FIB technology allows an effective preparation of the TEM lamellae on predefined areas (target preparation) and SEM observation during lamella preparation.[19]

All FIB preparations and SEM investigations were performed with a Quanta 3D FEG dual beam apparatus from FEI Company, USA. Gallium ion beam and electron beam operate separately (Figure 1). The angle between the electron beam and gallium ion beam is 52°. The point of coincidence at the sample working distance is 10 mm for the electron beam and 19 mm for the ion beam. To allow a vertical cutting by the focused ion beam, the sample has to be tilted at the angle of 52°. Then, observation of the sample with the electron beam occurs at an angle of 38° and that of the cross-section at an angle of 52°.

After screening the samples by conventional SEM at various magnifications, points of interest were selected for cross-sectional preparation (target preparation). Before target preparation, an additional carbon layer was deposited, using localized chemical vapour deposition, (CVD), wich is available in an FIB workstation. This additional layer protects the sample surface against scattered ions and redeposition. Also, in the cross-section, the surface becomes visible without contamination.

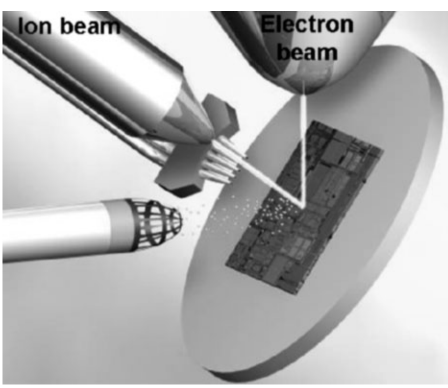

Figure 1.
Principle sketch of ion beam irradiation and electron beam observation in a dual beam Focused Ion Beam (FIB) workstation.

For investigations at low temperatures, the sample was cooled down inside the Polaron PPT 2000 (Quorum) sample cryo preparation unit and then transferred to the cryo stage of the Quanta 3D. The temperature measured on the sample holder was about 95 K. It has to be assumed that the temperature on the sample surface is slightly higher.

As a first cross-sectional preparation step at the predefined area of interest, coarse material ablation was performed with gallium ions accelerated with 30 kV and ion currents between 1 and 5 nA. Then, after this coarse milling step, lower beam currents of 50 to 300 pA were used for polishing the cross sections.

The ablation rate reached with the Gallium ion beam is much too low, to remove the upper foil with FIB technology. To investigate the structure of the gold layer, the upper foil must be removed. For that purpose, a welding seam with low mechanical stability, which was achieved by reducing the mechanical pressure between the foils during welding, was detached by mechanical peeling. At these samples, the gold nanolayer is not covered anymore and can be directly observed. This preparation is a compromise to investigate morphology changes at foil interconnections and gives hints about the morphology of a well-welded polymer foil.

Results and Discussion

Two ETFE foils were laser welded as described in the experimental section. Figure 2 depicts a photograph of the welded foils. The gray part in the middle shows the welding seam. Due to plasmon resonance, the deposited gold layer has a green colour. After Laser irradiation, the optical properties have changed dramatically. Figure 3 depicts the optical spectra taken between the positions x_1 to x_5 marked at Figure 2. The spectrum x_1 is taken from the unmodified foil with the gold nanolayer. The broad optical absorption with a maximum at about 840 nm is the result of the plasmon resonance of the deposited gold nanolayer.

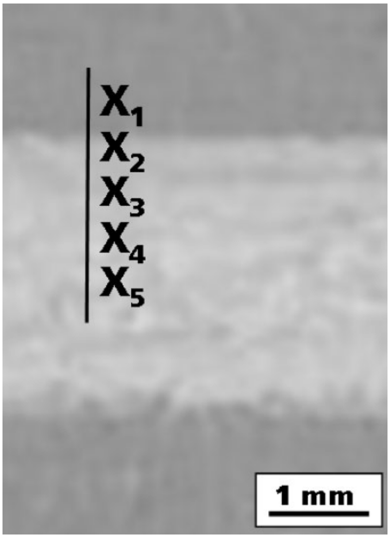

Figure 2.
Light microscope picture with the laser irradiated welding seam in the centre to describe different samples positions.

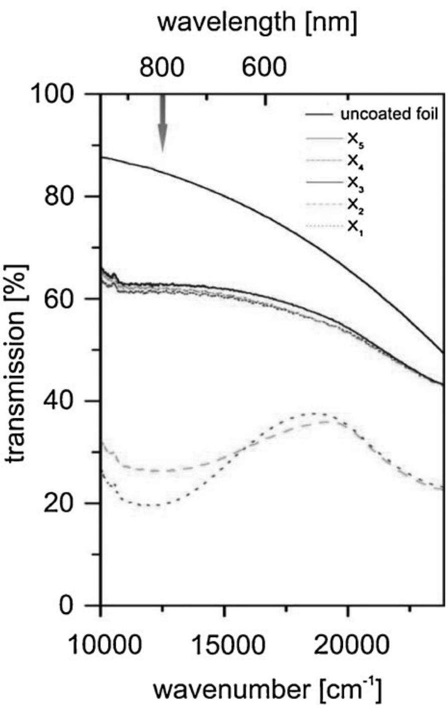

Figure 3.
Optical spectra of the uncoated ETFE foil and two laser welded ETFE foils at the positions described in Figure 2.

Based on spectral position of the plasmon resonance, it can be supposed that large nanoparticle or thin gold films were deposited on the ETFE foils. The spectrum at positon x_2 demonstrates that nanostructrual changes have partly occurred. After laser irradiation inside the welding seam (spectra x_3, x_4 and x_5), there is only a very weak plasma resonance absorption at about 900 nm. This indicates that substantial morphological changes of the gold nanolayer took place.

First, the changes of the gold nanolayer were observed with light microscopy. The optical absorption of the gold nanolayer makes this very easy. Figure 4 gives light microscope pictures of the ETFE foil at positions x1, to x5 (see Figure 2). At the micrograph of the non-irradiated pos. x1, the nanolayer is closed. Because of the different energy input during irradiation with the dispersed laser beam, various changes of the nanolayer have occurred.

At the picture taken from pos. x_2 to x_5, the gold nanolayer is already broken. In the pictures from pos. x_3 , x_4 and x_5, the gold nanolayer covers the copolymer structure. During laser irradiation, a polymer mold was formed and welding of the foils has occurred. Obviously, light microscopy can not give enough information about the gold nanolayer structure.

As described in the experimental part, the welding seam from Figure 2 was detached by peeling. Figure 5 depicts low magnification SEM micrographs of the lower foil, which was coated with the gold nanolayer before laser welding. The picture was taken at a low temperature to avoid surface modification by the thermal impact of the electron beam. The modification of the nanostructure is visible in the centre of the picture. Due to the low mechanical pressure, only parts of the polymer are molten during laser welding. This becomes much better visible in Figure 6.

Figure 6 gives two cryo SEM micrographs of the centre of the welding seam (position x_5) at two different magnifications. Now, the melting of the copolymer and the fixation to the other foils become

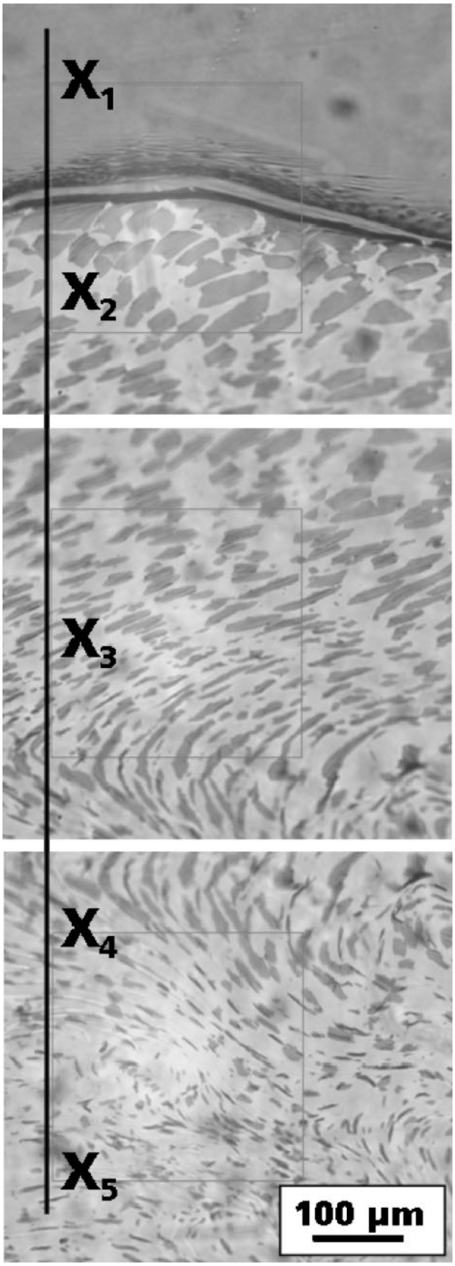

Figure 4.
Light microscopy (transmission mode) of the welding seam taken on positions x_1 to x_5.

conceivable. The sharp ''hollows'' are the result of the peeling of the upper foil. Between these polymer ''hollows'', the gold nanolayer becomes visible. The continuous gold film is broken in layers with dimensions in the micrometer region. Between these layers, the polymer interconnections with the other foil are formed. This partly connection is obviously the reason for the low mechanical stability. Now, signs for diffusion processes like coalescence or reshapening were found. However, the thermal load in the interface between the foil was high enough to melt this foil partly.

Finally, Figure 7 demonstrates the cross-sectional preparation of a selected part of the welding seam with FIB technology at cryo conditions. In the centre of the upper picture, the carbon layer, which was deposited to protect the sample surface, is depicted. Just in the middle of this protection layer, the ablation with the focused ion beam was started. The middle picture of Figure 7 shows the sample after cross-sectional preparation with the focused ion beam. Due to preparation at cyro conditions, there are no changes on the sample surface. The very sensitive fibre-like structures on the sample surface, which are a result of the polymer melting and the peeling of the foil after welding, were not modified or destroyed during FIB preparation. So, thermally inducted structural changes during ablation were avoided by the cryo conditions and the interfaces between the gold nanolayers and the polymer can be observed without preparation artefacts. The lower picture of Figure 7 demonstrates the cross-section of the sample with the gold nanolayer in the centre. Based on these micrographs, the thickness of the continuous gold nanolayer was determined at about 40 nm, which is in agreement to the thickness of the gold nanolayer measured during deposition by the quartz microbalance method. No nanostructural changes in the nanolayer were detected. This can be described in that way that the temperature in the polymer mold was not high enough to induce coalescence or reshapening of the gold nanolayer as supposed after investigation of the optical properties. Further, it becomes obvious that the Laser irradiation parameters during welding have to be changed

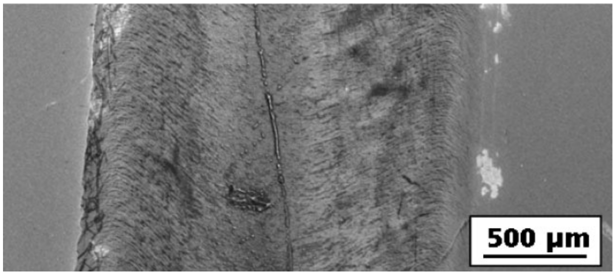

Figure 5.
SEM micrograph of the welding seam after peeling of the upper foil.

to get smaller isolated gold layers or to induce diffusion processes in the gold nanolayer. If this is realised, much more interconnections between the two foils will be formed and mechanical stability of the welding seams increase.

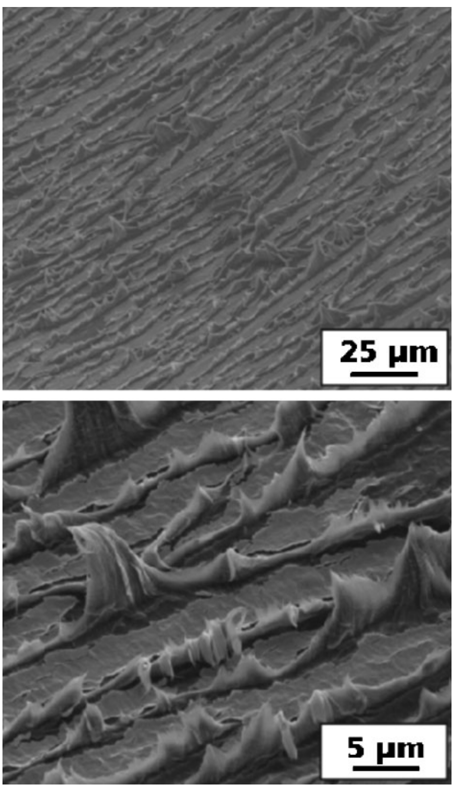

Figure 6.
SEM micrographs of the opened welding seam with the gold nanolayer.

Conclusion

The paper presents a first study of the microstructure of the laser welding seam, realised be using the optical absorption of metal nanolayer or metal nanoparticles. During cryo SEM investigation, performed together with FIB, it was found that the gold nanolayer was broken during laser welding and that the broken parts of the nanolayers show significant nanostrucutral changes. By only considering the optical spectra of welded seams, much more nanostructural changes were supposed. The investigations have demonstrated that, at cryo conditions, FIB preparation of polymers can be performed successfully without beam damages of sensitive polymer surface structures.

Because of the complicated cross-sectional preparation procedures, these first investigations were performed on welding seams with low mechanical stability to realize peeling of the foils in the interface. Up to now, welding seams with a breaking force of 89 N were realised. This value, measured on conventional strip samples, is similar to values realised with conventional thermal welding or laser welding with special dye absorbers. Otherwise, investigations of the nanostructure of the gold nanoplayer at the interface between the two foils are much more complicated. Investigations combining cryo microtomy with cryo FIB technology are under way. These investigations are part of a systematic study of laser irradiation para-

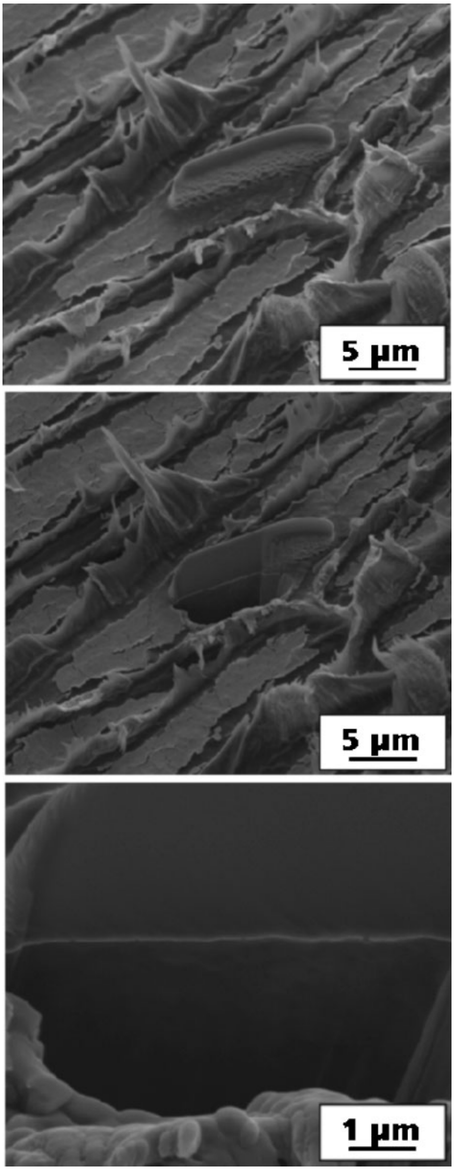

Figure 7.
SEM micrographs taken before and after cross-sectional preparation with FIB technology. The upper picture was taken before FIB preparation, the middle and the lower picture after cross-sectional preparation. There are no surface changes at the polymer samples before and after cryo FIB preparation.

meters and mechanical properties by using investigations of the optical properties and the gold nanostructure, which is in progress.

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[1] U. Kreibig, M. Vollmer, "*Optical Properties of Metal Clusters*", Springer Verlag, Berlin Heidelberg **1995**.
[2] K. Löschner, J. Lucas, S. Dauterstedt, E. Strogies, A. Heilmann, Patent pending **2008**.
[3] A. Heilmann, J. Werner, F. Homilius, F. Müller, Laser annealing of Plasma Polymer Metal Composite Films. *Journal of Adhesion Science and Technology*, **1995**, *9*, 1181–1191.
[4] A. Heilmann, *Polymer Films with Embedded Metal Nanoparticles*, Springer, Heidelberg **2002**.
[5] G. H. Michler, W. Lebek, "*Ultramikrotomie in der Materialforschung*", Carl Hanser Verlag, München **2004**.
[6] G. H. Michler, "*Electron Microscopy of Polymers*", Springer, Berlin **2008**.
[7] L. L. Ionescu-Vasii, P. M. Wood-Adams, E. Duchesne, G. L'Esperance, T. Karjala, P. Ansems, Morphological analysis of highly filled propylene/ethylene copolymers, *Journal of Applied Polymer Science*, **2007**, *105*, 3758–3772.
[8] C. Aubry, T. Trigaud, J. P. Moliton, D. Chiron, Polymer gratings achieved by focused ion beam, *Sythetic Materials* **2002**, *127*, 307–311.
[9] E. Pialat, T. Trigaud, V. Bernical, J. P. Moliton, Milling of polymeric photonic crystals by focused ion beam, *Materials Science and Engineering* **2005**, *C25*, 618–624.
[10] V. Luchnikov, M. Stamm, C. Akhmadaliev, L. Bischoff, B. Schmidt, Focused-ion-beam-assisted fabrication of polymer rolled-up microtubes, *Journal of Micromechanics and Microengineering* **2006**, *16*, 1602–1605.
[11] M. W. Moon, S. H. Lee, Y. J. Sun, K. H. Oh, A. Vaziri, J. W. Hutchinson, Wrinkled hard skins on polymers created by focused ion beam, *PNAS* **2007**, *104*, 1130–1133.
[12] S. Brunner, P. Gasser, H. Simmler, K. Ghazi Wakili, Investigation of multilayered aluminum-coated polymer laminates by focused ion beam (FIB) etching, *Surface & Coatings Technology*, **2006**, *200*, 5908–5914.
[13] D. J. Stokes, F. Morrissey, B. H. Lich, A New Approach to Studying Biological and Soft Materials Using Focused Ion Beam Scanning Electron Microscopy (FIB SEM)", *Journal of Physics: Conference Series* **2006**, *26*, 50–53.
[14] D. J. Stokes, T. Vystavel, F. Morrissey, Focused ion beam (FIB) milling of electrically insulating specimens using simultaneous primary electron and ion beam irradiation, *Journal of Physics D: Applied Physics* **2007**, *40*, 874–877.

[15] M. Neuber, J. Lucas, T. Hanke, A. Heilmann, in preparation.
[16] L. A. Giannuzzi, F. A. Stevie, (Eds.): *Introduction to Focused Ion Beams*: Springer Media Inc. **2005**.
[17] C. A. Volkert, A. M. Minor, Focused Ion Beam Microscopy and Micromaching, *MRS Bulletin* **2007**, *32*, 389–399.
[18] M. D. Uchic, L. Holzer, B. J. Inkson, E. L. Principe, P. Munroe, Three-Dimensional Microstructural Characterization Using Focused Ion Beam Tomography, *MRS Bulletin*, **2007**, *32*, 408–416.
[19] J. Mayer, L. A. Giannuzzi, T. Kamino, J. Michael, TEM Sample Preparation and FIB-Induced Damage'' *MRS Bulletin*, **2007**, *32*, 400–407.