

Positron Annihilation Study on Nanocrystalline Copper Thin Films Doped with Nitrogen

P.M. Gordo, M.F. Ferreira Marques and M.T. Vieira

1 Introduction

In the last decade a strong development in the nanomaterials field has been observed due to the unique and specific mechanical and physical properties of these nanomaterials comparatively to their coarser grain size materials [1–3]. On the other hand, thin metallic films play also an important role in many areas of the electronic industry for different applications, such as protective coatings [4], sensors [5] and contacts [6, 7]. Particularly, nanocrystalline copper is a promising material for automotive and electronic industries.

Among different fabrication processes, sputtering is well known for producing nanocrystalline thin films. However, maintaining the nanocrystalline character during processes or applications is still not an easy task due to the tendency towards grain growth exhibited by nanomaterials (copper presents a low tendency for nanocrystallinity due to the high adatoms mobility). On the other hand, the addition of solutes with a strong affinity for grain boundary segregation can inhibit grain growth, particularly during the manufacturing process, but it is still not well known the effects of impurities and dopants on the mechanical and physical properties of the nanomaterial. The presence of doping elements during the formation of sputtered metallic films could have an important role on the grain size decrease,

P.M. Gordo (✉) · M.F. Ferreira Marques
CFisUC, Department of Physics, University of Coimbra,
3004-516 Coimbra, Portugal
e-mail: pgordo@ci.uc.pt

M.F. Ferreira Marques
e-mail: fatima@coimbra.lip.pt

M.T. Vieira
CEMUC®, Department of Mechanical Engineering, University of Coimbra,
Coimbra, Portugal
e-mail: teresa.vieira@dem.uc.pt

particularly if they present low solubility in the metallic matrix, as is the case of N and C on Cu [8], and low tendency for the formation of compounds (Gibbs free energy > 0).

Few years ago, nanocrystalline copper thin films were successfully produced by magnetron sputtering through controlled additions of nitrogen in order to inhibit the grain growth [9]. The most likely mechanism for the production of nanosized grains was attributed to segregation of nitrogen to the copper grain boundaries anchoring their movements and avoiding grain growth. However, it was impossible to determine the localization of nitrogen, even after a detailed Transmission Electron Microscopy (TEM) study. In fact, Energy Dispersive Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS) analysis did not reveal any vestiges of nitrogen inside the grains or in the grain boundaries [9].

Positron annihilation spectroscopy is a well established tool for the study of electronic and defect properties of solids [10–12]. The crux of this technique is that in solid materials positrons are efficiently trapped at defects such as vacancies or voids, which makes them a very sensitive probe for studying these defects. After trapping the positron will annihilate with an electron from the immediate surrounding of the defect, thus producing two 511 keV gamma-photons. The defect-related information is obtained from properties such as the lifetime of the positrons, the Doppler broadening of the photo-peak, or the angular-correlation between the two photons. Furthermore, the development in slow positron beam methods allows the extension of traditional techniques to investigation of thin films, layered structures and surfaces [12, 13]. Slow positrons are produced in an ultrahigh vacuum environment by the slowing down of positrons from a 5 mCi β^+ emitting ^{22}Na source in a 4 μm thick polycrystalline tungsten moderator foil and subsequent reemission of the positrons from the surface of the moderator. The positrons are magnetically guided and near the samples are accelerated by an electric field to kinetics energies ranging between 50 eV and 25 keV entering into the sample. Varying the incident energy results in a depth-resolved study of materials properties in the first 1.5 μm surface region of the sample. (For full description of the Coimbra variable energy positron beam, see Ref. [14].)

When positrons are implanted in a sample, the stopping profile is generally assumed to be Makhovian with a mean implantation depth approximately proportional to $E^{1.6}$, where E represents the positron energy [15]. After slowing down and some diffusion the positrons implanted in the sample either annihilate in a defect-free region or become trapped in a defect and annihilate there. The energy of the annihilation radiation of the positron may deviate slightly from the value of 511 keV as a result of the nonzero value of the momentum of the electron at the moment of annihilation (Doppler broadening). The electron momentum distribution in defects is in general different from the one in defect-free material, resulting in a different Doppler broadening of the 511 keV annihilation peak. The momentum distribution is characterized by the line shape parameters $S(W)$ [12] defined as the relative number of annihilation events in the centroid (wings) of the 511 keV line. Annihilations with low (high) momentum electrons fall to the energy window of

$S(W)$. Therefore, mainly valence electrons contribute to S whereas only core electrons are represented in W . The annihilation parameters at the defect can be used as fingerprints of the open volume of the defects. The larger the open volume, the lower the core annihilation parameter and the higher the valence annihilation parameter. In general the S value is also proportional to the defect concentration in the sample (although the proportionality is not necessarily linear), i.e., a higher S corresponds to a higher defect concentration. A positron in a defect sees a different electron density than in a defect-free material, owing to the lower concentration of core electrons. Generally, the most important effect of appreciable positron trapping is a narrowing of the momentum curves and, therefore, a narrowing of the 511 keV peak width, which is equivalent to an increase of the S parameter [12]. The positron diffusion length is also dependent on the defect density. A higher defect concentration leads to a shorter diffusion length.

S - and W -parameters measurements as a function of incident positron energy give an indication of the depth-resolved defect regions in a sample [13].

Since nanocrystalline materials due to the small grain size contain a large free volume fraction associated with grain interfaces, vacancies and nanopores [14–17], which constitute trapping centers for positrons, can be study with positrons.

In the present study we employ positron annihilation Doppler broadening measurements to characterize the dependency of nitrogen content on the open volume defects present in nanocrystalline copper thin films and try to identify the possible nitrogen location in these nanomaterials. The experimental details are presented in Sect. 2. In Sect. 3 we present the results concerning the identification of the positron trapping centers in the films. The conclusions are summarized in Sect. 4.

2 Experimental

Copper and nitrogen doped copper thin films were growth onto glass substrate by dc magnetron sputtering using a pure copper target. The nitrogen doped copper films were produced in reactive mode using 1:60, 1:30 and 1:2 nitrogen/argon partial pressure ratios (P_{N_2}/P_{Ar}). The thickness of films was measured to be between 2–3 μm . The deposition was carried out at 0.3 Pa total pressure and applying to the copper target a constant power density of $3.33 \times 10^4 \text{ Wm}^{-2}$. During the deposition, and to avoid the grain growth, the temperature of the substrate was maintained lower than 373 K by promoting the heat flow through the substrate's holder. The sputtering chamber was evacuated to 2×10^{-4} Pa before admitting pure argon and nitrogen gases.

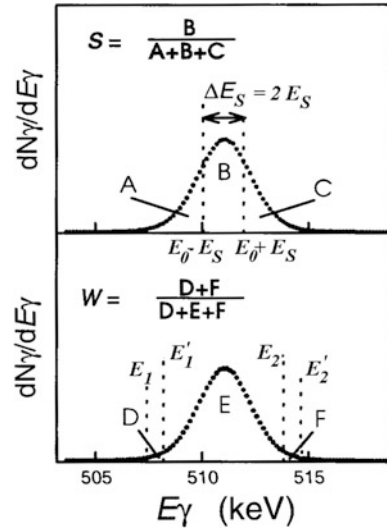
All the films studied in this work are identical to those used in Ref. [9].

Carbon, hydrogen, nitrogen and sulphur contents of the N doped films were determined by elemental analysis using a Fisons EA1108 mass spectrometer.

In situ positron annihilation Doppler broadening measurements as a function of energy were carried out at room temperature with a magnetically guided slow positron beam. The energy range of the implanted positron was between 0.1 and 25 keV. This energy range corresponds to a mean penetration depth, $\{z = 45 [E(\text{keV})]^{1.6} \text{ \AA}\}$, of up to 0.8 μm in copper (assuming that the copper film density is similar to bulk copper density, 8.92 g.cm^{-3}). Positrons are stopped well before the substrate since all the films are more than 2 μm thick. For each positron energy, the 511 keV annihilation line was measured using an intrinsic Ge detector with an energy resolution of 1.2 keV at 497 keV gamma energy (^{103}Ru). The measurements were performed in the Coimbra Variable Energy Positron beam. This facility provides positrons with a typical flux of $10^2 \text{ s}^{-1}\text{cm}^{-2}$. The background pressure in this vacuum system is about 10^{-7} Torr. The structural properties of the films are investigated by implantation of monoenergetic positrons. After thermalization the positron diffuse through the material. In defective materials most of them will be trapped at defects. Ultimately, they annihilate with an electron, thus producing two gamma-photons of about 511 keV. The information on the defects is obtained from the Doppler broadening of the photo-peak, which is related to the momentum of the annihilated particles.

The photo-peak is characterized using two parameters, the shape parameter (S) and the wing parameter (W), defined in Fig. 1. The shape parameter is associated with annihilation with low momentum (valence) electrons [12]. The wing parameter corresponds to annihilation with high momentum (core) electrons [12]. Thus the information about the structure of defects of the thin films is provided by the energy-dependent data, $S(E)$ and $W(E)$.

Fig. 1 Definition of shape parameter S and wing parameter W of the photo-peak. The areas A, B, C, D, E, F indicate sections defined with the aid of a fixed integration window (ΔE_S , E_1 and E_2). The figure shows a typical experimental spectrum



3 Results and Discussion

The introduction of nitrogen in the sputtering chamber was successfully used to produce nanocrystalline copper thin films. The presence of nitrogen, even in small amount, results in a reduction in the grain size and, simultaneously, in a homogeneous grain size distribution as observed by Transmission Electron Microscopy [9].

In Table 1 is presented the nitrogen content and the grain size of the films as a function of the nitrogen/argon partial pressure ratio during the film deposition. A continuous grain size decrease down to 30 nm is observed as the nitrogen content increases up to 3.5 at.%. For the highest nitrogen content a slight grain size increase is observed, which might be attributed to the formation of the Cu_3N nitride phase. In fact, as previously reported in reference [9], for the highest $P_{\text{N}_2}/P_{\text{Ar}}$ ratio studied a shoulder corresponding to the (111) plane of the Cu_3N phase is identified, besides the fcc Cu phase. It must be reported here that the nitrogen content presented in Table 1 is an estimated average value, since the observed nitrogen content value at the top surface of the film is higher than that observed at the bottom where the film began to grow. This gradient depends on the nitrogen content and it is larger for the films richer in nitrogen.

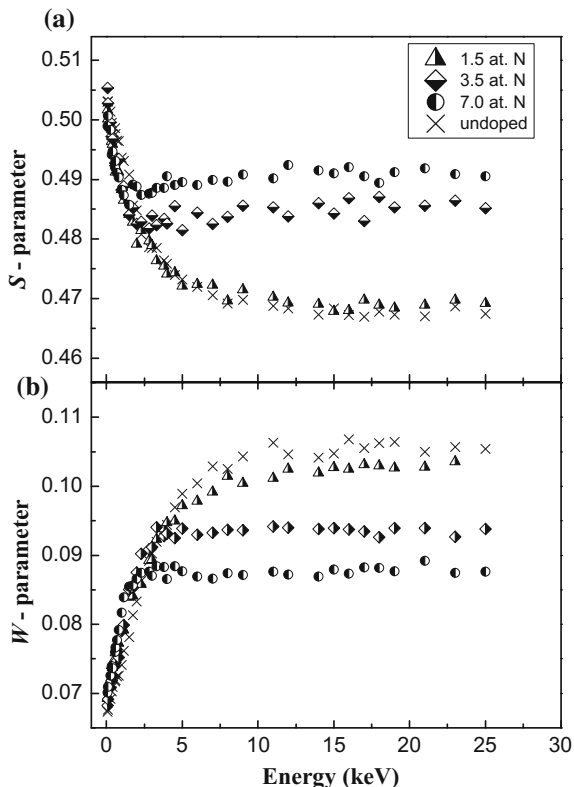
In Fig. 2 the Doppler S parameter and W parameter values—as a function of positron implantation energy—are shown for pure and for different nitrogen content Cu thin films. As can, immediately, be observed the films with nanocrystalline structure (3.5 and 7.0% of nitrogen content, respectively) reveal a quite different $S(E)$ and $W(E)$ curves than the films with microstructure (pure copper and 1.5% nitrogen content). Particularly, far from the surface of the film (positron energy higher than 15 keV) the S -parameter value, Fig. 2a, is significantly higher for the nanocrystalline films comparatively to the value of the same parameter for the films with larger grain size.

The effect of increasing of the S -parameter value in the region of the film is related to the presence of the large free volume fraction of these nanocrystalline films comparatively to the microcrystalline ones, namely the presence of vacancy type defects as will be discussed later. Also, Fig. 2a shows that the film with lower nitrogen content has a similar $S(E)$ curve as the pure copper film meaning that the positron annihilates with pure Cu film characteristics. Analogous behaviour is observed in $W(E)$ curve.

Table 1 Nitrogen content and grain size of pure and N doped Cu thin films deposited onto glass substrate under different N_2/Ar partial pressure ratio

| $P_{\text{N}_2}/P_{\text{Ar}}$ | Nitrogen average content (%) | Grain size (nm) |
|--------------------------------|------------------------------|-----------------|
| 0 | – | 480 |
| 1/60 | 1.5 | 140 |
| 1/30 | 3.5 | 30 |
| 1/2 | 7.0 | 50 |

Fig. 2 Doppler S and W parameters versus incident positron energy for pure and nitrogen doped copper thin films with 1.5, 3.5 and 7.0% average nitrogen content
a S —parameter,
b W —parameter



Using the VEPFIT code [18] to fit the $S(E)$ curves showed in Fig. 2a, the characteristic Doppler parameter, S_{film} , of each film were obtained and, also, the positron diffusion length. Table 2 shows these parameters for all the films. The analyses were performed considering one or two layers to characterize the films: the films with microstructure (pure and with 1.5% N) were well defined considering only one layer and for the films with higher content of nitrogen a second layer (top layer, immediately below the surface) was needed to consider. So, for the pure and low doped films the positron annihilate with 2 different characteristic S —parameter values: surface and film; and for the high doped films a third characteristic S —parameter value was needed, related to the top layer immediately below the surface. The normalization of the S —parameter values of the films, S_{film} , to the reference pure copper (undoped) film value gives 1.001, 1.038 and 1.050 for the films with 1.5, 3.5 and 7.0% nitrogen content, respectively. The increasing observed in the S parameter for the films with higher nitrogen content is a typical evidence of the presence of open volume type defects. The comparatively small values of the diffusion length of the positron is an indication that positrons annihilate in a saturation trapping regimen: all positron annihilate after to be captured in some type of open volume defect.

Table 2 Positron related parameters derived from VEPFIT analysis for pure and N doped Cu thin films

| Film | S_{lay} | L_{lay} (nm) | d_{lay} (nm) | S_{film} | L_{film} (nm) |
|------------|------------------|-----------------------|-----------------------|-------------------|------------------------|
| Undoped | – | – | – | 0.4679 (2) | 23 (1) |
| 1.5% at. N | | | | 0.4691 (9) | 21 (2) |
| 3.5% at. N | 0.4388 (4) | 12 (3) | 17 (3) | 0.4856 (3) | 51 (17) |
| 7.0% at. N | 0.4523 (5) | 10 (3) | 15 (2) | 0.4911 (3) | 23 (9) |

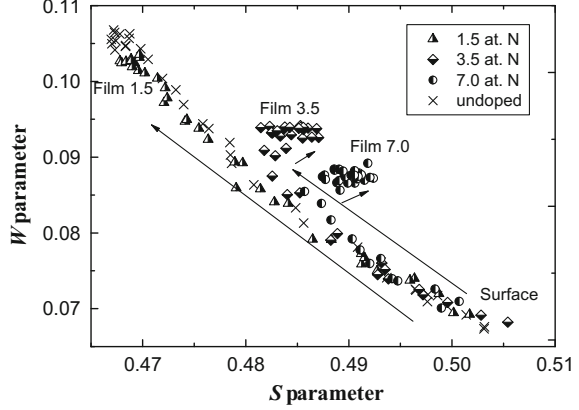
The determined parameters are the shape-parameter S for the top layer, S_{lay} , and film, S_{film} , and thickness of top layer, d_{lay} , and diffusion length of positrons in the top layer, L_{lay} , and in the film, L_{film} . The surface S —parameter is not presented. The errors are also shown between parentheses

For nanocrystalline metallic materials, it has been reported in the literature [16, 17, 19] the observation, mainly, of two positron annihilation lifetimes associated with vacancy sized defects at the interfaces between grains ($\tau_2 \sim 150\text{--}200$ ps) and vacancy clusters or nanovoids ($\tau_3 \sim 300\text{--}400$ ps) at the intersection of interfaces (triple-lines). Sometimes, a third components is referred ($\tau_4 \sim 1\text{--}2$ ns) as due to the large pores or missing grains [20].

The trapping of positrons at the interfaces between the grains it is expected to act as a shallow trapping center [12, 21] and the S parameter observed from the annihilation of positron trapped in these centers does not differ much from the free nitrogen copper film, which can explain the similar S_{film} values observed for pure Cu and 1.5% N doped Cu film. Also, the positron diffusion length are quite similar (23 ± 2 and 21 ± 2 nm, respectively) in both films. In fact this value for the positron diffusion length is much smaller than the one observed in defect-free metals (around 100 nm, [17, 19]) and since the grain size for these films are 480 and 140 nm respectively, the results suggest that some king of positron trapping center (vacancy type defect) must be present in these films. On the contrary, a high S_{film} values is observed for both 3.5 and 7.0% N doped films. These results reveal the presence of vacancy defects, like vacancy clusters or nanovoids at the intersection of interfaces (triple-lines) as observed in positron lifetime spectroscopy ($\tau_3 \sim 300\text{--}400$ ps) experiments for nanocrystalline Cu [17, 19]. In fact, the existence of these nanovoids was, clearly, observed in the our film with 7.0% nitrogen content by High Resolution Transmission Electron Microscopy (HRTEM) as reported in reference [9]. The fitting of the $S(E)$ curves requires, at least for the nanocrystalline Cu thin films (3.5 and 7.0% of N content), a minimum of two layers to describe the films, which suggested a non-uniform film structure in depth. It can be seen in Fig. 2, for incident positron energy at around 2.5 keV, a minimum in the $S(E)$ curve for these films. The fitted thickness of the first top-layer is 15–17 nm and the positron diffusion length in this layer is around 10–12 nm. This result suggests a strong trapping of positron in this region with different positron annihilation characteristics. The application of the S - W plot analysis allows clarifying this interpretation.

In Fig. 3 we have plotted the $S(E)$ and $W(E)$ data of the different copper thin film as a trajectory in the S — W plane, using the implantation energy as a running parameter. The arrows denote the direction of increasing implantation energy.

Fig. 3 S - W trajectories for positrons implanted in pure and nitrogen doped copper thin films with 1.5, 3.5 and 7.0% average nitrogen content. Arrows indicate the direction of increasing implantation energy



The different trapping layers are characterized by (S, W) coordinates instead of a single S -value. For example, for the high-energy implantation all positrons annihilate with the S and W values characteristics of the film. In the S - W plane this is seen from the clustering of the experimental data.

The convenience of interpretation of the S - W plot stems from the linearity property of S and W which is a consequence of the particular choice of their definition (Fig. 1) [22]. The value of this property for the interpretation of the S - W trajectory can be seen as follows. Suppose that we have a system where the positrons annihilate in two different trapping layers only, which will be designed A and B . These layers are situated at different depth and are characterized by different (S, W) coordinates, (S_A, W_A) and (S_B, W_B) . The implanted positrons thus will be distributed over the A and B layer. This distribution can be varied by changing the implantation energy. Because of the linearity property of the shape and wing parameters, such a variation corresponds to a straight line trajectory in the S - W plane running from the coordinates (S_A, W_A) towards (S_B, W_B) ,

$$S_M = f_A S_A + (1 - f_A) S_B \quad (1)$$

$$W_M = f_A W_A + (1 - f_A) W_B \quad (2)$$

where f_A denotes the fraction of positrons trapped in layer A and S_M and W_M are the measured values. The presence of an additional, trapping layer with another depth distribution can now be immediately established from the trajectory: it should be curved unless the characteristic (S, W) coordinates of this trapping layer is accidentally located on the line $(S_A, W_A) - (S_B, W_B)$.

With the aid of the above interpretations of straight and curved trajectories, we can easily explain our experimental data shown in Fig. 3. The S - W trajectories for the pure copper and the 1.5% nitrogen content films show a linear behavior and this can be interpreted as the positron annihilates either with the characteristic values of the surface or of the characteristic values of the film: the two annihilation places are

surface and film. On the other hand, for the 3.5 and 7.0% nitrogen content copper films the trajectory deviates from the straight line and shows a curved trajectory revealing the existence of a third layer. This result is consistent with the analyses referred above related to the fit of the $S(E)$ curve that has revealed the existence of a top-layer with a thickness of the about 15–17 nm. At very low energy the positron annihilate in the surface of the film or in that top layer states and for higher energies the positrons annihilate with the characteristic values of the film (clustering of points).

In our opinion the reduction in the S parameter in the sub-surface region comparatively to the S_{film} value must be related to the partial occupancy of the free volume (vacancy clusters or nanovoids) with nitrogen. In fact, this behaviour agrees with the observed gradient in nitrogen content reported before and it seems to indicate that during the film deposition some of the nitrogen is released from the bottom to the top of the film surfaces as was also reported in [23, 24]. This hypothesis can be, eventually, confirmed by positrons measuring the $S(E)$ and $W(E)$ curves in the bottom surface of the films, which will be one of the next steps of the investigation.

4 Conclusion

The presence of nitrogen during the formation of Cu films by magnetron sputtering had an important role decreasing the grain size and in the production of nanocrystalline thin films. The positron annihilation measurements have identified the interfaces between the grains and the nanovoids at the intersection of interfaces as the main positron trapping centers and, consequently, the main lattice defects in these films. A non-uniform film structure was also observed and it was related to the gradient of the nitrogen content in depth. The reduction observed in the S parameter near the top surface of the nitrogen doped films suggests the partial occupancy of the open volume defects with nitrogen.

References

1. Lu, L., Shen, Y., Chen, X., Qian, L., Lu, K.: Ultrahigh strength and high electrical conductivity in copper. *Science* **304**, 422–426 (2004)
2. Kumar, K.S., Swygenhoven, H.Van, Suresh, S.: Mechanical behavior of nanocrystalline metals and alloys. *Acta Mater.* **51**, 5743–5774 (2003)
3. Su, J.Q., Nelson, T.W., Sterling, C.J.: A new route to bulk nanocrystalline materials. *J. Mater. Res.* **18**, 1757–1760 (2003)
4. Rohella, R.S., Swain, B.C., Murty, J.S.: Cathodic protection system: Protecting under-water steel piles of an iron ore berth. *Anti-corrosion Meth. Mater.* **38**, 4–7 (1991)

5. Dimitrov, D.A., Zahariev, A.L., Georgiev, J.K., Kolev, G.A., Petrinski, J.N., Ivanov, T.: Thin film platinum resistance thermometers: calibration and mathematical description of T(R) function. *Cryogenics* **34**, 487–489 (1994)
6. Tokura, H., Window, B., Neely, D., Swan, M.: Microstructure and mechanical properties of sputtered platinum films. *Thin Solid Films* **253**, 344–348 (1994)
7. Peto, G., Anderson, T.: Preparation of a Pt-GaAs Schottky contact by ion plating. *Solid State Electron.* **34**, 591–592 (1991)
8. Hansen, M., Anderko, K. (eds.): *Constitution of Binary Alloys*. McGraw-Hill, New York (1958)
9. Calinas, R., Vieira, M.T., Ferreira, P.J.: The effect of nitrogen on the formation of nanocrystalline copper thin films. *J. Nanosci. Nanotechnol.* **8**, 1–6 (2008)
10. Brandt, W., Dupasquier, A.: *Positron Solid State Physics*. North Holland, Amsterdam (1983)
11. Dupasquier, A., Mills Jr., A.P.: *Positron Spectroscopy of Solids*. IOS, Amsterdam (1995)
12. Krause-Rehberg, R., Leipner, H.S.: *Positron Annihilation on Semiconductors—Defect Studies*. Springer, Berlin (1999)
13. Ishii, A.: *Positrons at Metallic Surfaces*. Trans Tech, Aedermannsdorf (1992)
14. de Lima, A.P., Lopes Gil, C., Gordo, P.M., Duarte Naia, M.: Initial results with a variable energy positron system at coimbra. In: *OECD/NEA—Workshop Proceedings on Ion and Slow Positron Beam Utilisation*, pp. 121–128 (1998)
15. Asoka-Kumar, P., Lynn, K.G.: Implantation profile of low-energy positrons in solids. *Appl. Phys. Lett.* **57**, 1634–1635 (1990)
16. Schaefer, H.-E., Würschum, R., Birringer, R., Gleiter, H.: Structure of nanometer-sized polycrystalline iron investigated by positron lifetime spectroscopy. *Phys. Rev. B* **38**, 9545–9554 (1988)
17. Eldrup, M., Sanders, P.G., Weertman, J.R.: Positron annihilation study of the influence of grain size and purity on the annealing behaviour of nano-crystalline copper. *Mat. Sci. Forum* **255–257**, 436–438 (1997)
18. van Veen, A., Schut, H., de Vries, J., Hakvoort, R.A., Ijpma, M.R.: *Positron Beams for Solids and Surfaces*, pp. 171–198. AIP, New York (1990)
19. Mizuno, M., Kihara, T., Araki, H., Shirai, Y., Onishi, T.: Identification of lattice defects in Cu thin films by positron annihilation spectroscopy. *Phys. Stat. Sol. (c)* **4**, 3550–3553 (2007)
20. Würschum, R., Scheytt, M., Schaefer, H.-E.: *Nanocrystalline Metals and Semiconductors Studied by Positron Lifetime Spectroscopy*. *Phys. Stat. Sol. (a)* **102**, 119–126 (1987)
21. Kuriplach, J., Melikhova, O., Hou, M., Petegem, S.Van, Zhurkin, E., Šob, M.: Positron annihilation in vacancies at grain boundaries in metals. *Appl. Surf. Sci.* **255**, 128–131 (2008)
22. Asoka-Kumar, P., Lynn, K.G., Welch, D.O.: Characterization of defects in Si and SiO₂ – Si using positrons. *J. Appl. Phys.* **76**, 4935–4982 (1994)
23. Ji, A., Li, C., Du, Y., Ma, L., Song, R., Huang, R., Cao, Z.: Formation of a rosette pattern in copper nitride thin films via nanocrystals gliding. *Nanotechnology* **16**, 2092–2095 (2005)
24. Nosaka, T., Yoshitake, M., Okamoto, A., Ogawa, S., Nakayama, Y.: Copper nitride thin films prepared by reactive radio-frequency magnetron sputtering. *Thin Solid Films* **348**, 8–13 (1999)

Materials Design and Applications

Da Silva, L.F.M. (Ed.)

2017, X, 431 p. 269 illus., 175 illus. in color., Hardcover

ISBN: 978-3-319-50783-5