The transient electrical conductivity of W-based electron-beam-induced deposits during growth, irradiation and exposure to air

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Abstract

W-based granular metals have been prepared by electron-beam-induced deposition from the tungsten hexacarbonyl \( \text{W(} \text{CO}_6 \text{)} \) precursor. In situ electrical conductivity measurements have been performed to monitor the growth process and to investigate the behavior of the deposit under electron beam post-irradiation and by exposure to air. During the first part of the growth process, the electrical conductivity grows nonlinearly, independent of the electron beam parameters. This behavior is interpreted as the result of the increase of the W-particle’s diameter. Once the growth process is terminated, the electrical conductivity decreases with the logarithm of time, \( \sigma \sim \ln(t) \). Temperature-dependent conductivity measurements of the deposits reveal that the electrical transport takes place by means of electron tunneling either between W-metal grains or between grains and trap sites in the matrix. After venting the electron microscope the electrical conductivity of the deposits shows a degradation behavior, which depends on the composition. Electron post-irradiation increases the electrical conductivity of the deposits.

Supplementary data are available from stacks.iop.org/Nano/20/195301

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electron-beam-induced deposition (EBID) is a high resolution one-step technique used to deposit and to pattern two- and three-dimensional micro- and nanostructures [1]. The importance of EBID is rapidly increasing in applied science and fundamental research [2]. On the one hand, the possibility of direct writing makes EBID a promising alternative to nanolithography and a useful tool for mask repair. On the other hand, the capability to produce deposits from many different precursors with tunable electrical properties makes this technique attractive for the development of new materials. EBID is based on the interaction of an electron beam with a substrate which is covered by adsorbed precursor molecules and which contain the metal or semiconductor to be deposited. The electrons dissociate the precursor molecules into a volatile component, which leaves the surface, and into a non-volatile one, which forms the deposit. The deposits consist of a disordered array of crystalline metallic nanoparticles with diameters between about 1–5 nm embedded in an insulating matrix. The metal volume fraction, i.e. the average particle size and the interparticle distance, can be varied by tuning the electron beam parameters (mainly beam current, acceleration voltage and dwell time).

In situ electrical conductivity measurements of granular materials prepared by EBID or IBID (ion-beam-induced deposition) are valuable in order to study the growth process and the response of the material during post-irradiation and exposure to air. By means of these measurements information about the electrical transport properties, the microstructure and the chemical and physical stability of the deposit are deduced. In the literature, in situ electrical measurements of IBID and EBID deposits are rare [2]. The electrical behavior of EBID deposits from acrylic acid has been monitored by means of two-probe measurements [2]. Recently an ageing process has been monitored in platinum-based nanostructures [3]. The
authors report a continuous decrease of conductivity over a time range of many days. Studies performed by using W(CO)₅ as a precursor are known for deposits produced by IBID [4] and EBID [5, 6]. The investigation of Hoyle et al [5, 6] represents an important reference for the present study. In their work the authors prepared structures for electron beam energies between 2 and 20 keV. They investigated in situ the electrical conductivity of the deposits and, by means of transmission electron microscopy (TEM), their microstructure. It is the purpose of the present paper to further investigate the properties of W-based deposits from the W(CO)₅ precursor by performing in situ transient electrical conductivity measurements during deposition, post-irradiation and exposure to air.

2. Experimental details

To prepare our samples we used a dual-beam SEM/FIB microscope (FEI, Nova Nanolab 600) with Schottky electron emitter and an ultimate resolution of 1 nm. In this system the electron beam power can be continuously tuned by means of continuous variation of the beam energy and pre-defined discrete values of the beam current. The microscope is equipped with a gas injection module which introduces the W(CO)₅ gas precursor via a 0.5 mm diameter capillary in close proximity to the focus of the electron or ion beam on the substrate surface. The molecular flux is estimated to be 6 × 10¹⁹ cm⁻² s⁻¹ at the crucible temperature of 54 °C, as estimated from equation (2.11) of [2]. EBID structures were grown on an Si (p-doped)/SiO₂ (300 nm) substrate. The substrates were pre-patterned with 120 nm thick Au/Cr contacts defined by UV photolithography. Strip-like patterns were deposited by repeatedly rastering over the structure at fixed dwell time per pixel and pitch between pixels. The loop time is defined as the time necessary to raster the structure once. The pattern was rastered in a serpentine fashion. For details concerning the composition, the geometry and the beam parameters used during deposition see table 1. In figure 1 we show a scanning electron microscope (SEM) image of three deposits for two-probe electrical measurements. This technique was chosen after having verified that the influence of the contact resistance between electrodes and deposits is below about 3%. Our chips are prepared to allow measurements for up to 12 deposits. After deposition in situ energy-dispersive x-ray analysis (EDX) at 5 keV electron beam energy was performed in order to determine the material composition of the deposit. The low beam energy was chosen to avoid excitation of x-ray fluorescence in the substrate material. This was verified by Monte Carlo simulations of the electron trajectories for the given thicknesses and compositions of the deposit¹, see supplementary figures S1 and S2 (available at stacks.iop.org/Nano/20/195301). For in situ transient electrical conductivity measurements a Keithley Sourcemeter coupled with a multiplexer was used to perform current measurements at fixed bias voltage. The conductivity was deduced from the known dimensions of the deposits. The length l, width w and height h of each sample were determined by direct inspection of the SEM images. The maximum geometry-dependent error for the conductivity data amounts to about 35%. Finally, temperature-dependent measurements of the electrical conductivity in the temperature range 1.8–265 K were performed in a variable-temperature insert mounted in a ⁴He cryostat.

¹ Casino (Monte Carlo simulation of electron trajectories in solids) v2.42.
3. Measurements

3.1. Deposition parameters and EDX characterization

In figure 2 we report the results of the composition analysis performed by means of EDX for the samples used in this work. The deposits have been obtained with a variable electron beam energy and current in the range $4 \text{ keV} \leq E \leq 20 \text{ keV}$ and $0.25 \text{ nA} \leq I \leq 6.6 \text{ nA}$, respectively. The corresponding electron beam power varied between $5 \text{ nA keV} \leq p \leq 26 \text{ nA keV}$. Within this range the deposits are granular with a W content which increases linearly between 8.1 and 38.7 at.%. In the left inset of figure 2 we plot the conductivity versus the dose per loop. For high doses per loop the conductivity lies in the range between approx. 9300 and 18 000 $\Omega^{-1} \text{ m}^{-1}$. These values are in agreement with the ones reported by Hoyle et al. [5, 6]. For smaller beam power we measure a strong decrease of the conductivity which reaches 17 $\Omega^{-1} \text{ m}^{-1}$ at 65 C $\text{m}^{-2}$. This value is one order of magnitude smaller than the one reported in [5, 6] for comparable dose per loop. On the right-hand side of figure 2 we plot the ratio between oxygen (or carbon) and tungsten ([O]/[W] or [C]/[W]) content versus the tungsten content for each deposit. The ratio ([O] + [C])/[W] is also plotted. For W content equal to 8.1 at.% we obtain ([O] + [C])/[W] = 11.4. This value is close to the one deducible from the stoichiometry of W(CO)$_6$ if one were to assume that the CO molecules do not dissociate. By increasing the beam power the W content increases, whereas the carbon and oxygen content decrease. Additional information can be deduced from the ratio [C]/[O] (see the inset). For low doses we find [C]/[O] > 1, which shows that the composition of the matrix is dominated by carbon. The [C]/[O] ratio shows a peak for a W content of approx. 15 at.% and then it decreases towards 1. By means of TEM measurements Hoyle et al. [5] found amorphous material for deposits prepared with a dose per loop smaller than 500 C $\text{m}^{-2}$. For higher doses they found W-containing nanocrystals consistent with the high temperature $\beta$ phase of tungsten carbide ($\beta$-WC$_{1-x}$). The nanocrystal size was estimated to be less than about 3 nm. From the EDX analysis of our deposits we point out that the [W] content increases with increasing beam power or with increasing dose per loop.

3.2. Measurements during growth and relaxation

In figure 3 we show transient electrical conductivity measurements during the growth of deposits with a W content of 8.1 at.% (sample #1), 14.7 at.% (sample #4) and 38.7 at.% (sample #9). At the time $t = 10$ s the gas precursor enters the vacuum chamber. The conductivity changes at a rate $\sigma' = \sigma/t$, which increases monotonically with time during the deposition of all samples. Sample #9 shows a rapid increase of $\sigma'$ in the first seconds of deposition, which we attribute to the formation of the first layer of the deposit. In the first 5 s $\sigma'$ follows a power law of the form $\sigma' = t^\alpha$, with $\alpha = 3$. After that, $\sigma'$ drastically decreases, tending to become constant, as can be expected if the thickness of the deposit grows linearly with time. $\sigma'$ for the deposits with 8.1 at.% and 14.7 at.% metal content follows a power law of the form $\sigma' \sim t^\alpha$, with $\alpha = 1.86$ and $\alpha = 1.43$, respectively. For sample #1 $\sigma'$ follows this power law during the whole deposition process, while for sample #4 it shows a decrease after about $t = 10^3$ s. The fit to sample #4 was made between 300 and 1000 s. In this range the growth rate is lower than in the first 300 s of deposition, which we excluded from the fit because of the high scatter of the experimental data points. Therefore it is not surprising that the result of the fit gives for $\alpha$ a value larger for sample #1 than for sample #4, which is counterintuitive since we expect higher growth rate for deposits with higher metal content.
Figure 3. Electrical conductivity measured during the growth of samples #1 (8.1 at.% W), #4 (14.7 at.% W) and #9 (38.7 at.% W), respectively. In each case, the deposition was started at \( t = 10 \) s. The data points in the inset for sample #9 show that, after an initial nonlinear growth, the conductivity tends to increase linearly with time. The conductivity of samples #1 and #4 is nonlinear during the whole deposition time considered, which is due to the lower growth rate of these deposits. The electrical conductivity of each sample decreases once the deposition process is terminated, as indicated by the arrows.

The growth process terminates with the simultaneous shut-off of the electron beam and the precursor gas supply. Correspondingly, the conductivity starts to decrease (see figure 3). The relaxation of the conductivity can be attributed to the migration of excess electrons injected by the electron beam towards the electrodes. In figure 4(a) we depict the relaxation for samples #1, #4 and #9. The conductivity relaxation follows a logarithmic time dependence, i.e. \( \sigma = b \ln(t) \). With suitable choice of the parameter \( b \), this formula can be used to fit the relaxation of all the deposits. The velocity of the relaxation depends on the deposits’ composition. In particular, we notice that deposits with lower W content relax more rapidly than deposits with higher W content. This information is summed up in figure 4(b) for all the samples prepared in this work.

3.3. Measurements during venting the microscope

Transient electrical conductivity measurements during exposure to air were performed after deposition by venting the electron microscope. The result of these experiments are summarized in figure 5 where we plot the normalized conductivity versus time for various deposits. The venting procedure starts at \( t = 60 \) s, when \( N_2 \) gas enters the chamber. The conductivity of the deposits starts to decrease with a rate which depends on the metal concentration. In particular, the lower the metal con-

Figure 4. (a) Relaxation of the conductivity after the end of the deposition process. The conductivity decreases with the logarithm of the time, \( \sigma = b \ln(t) \). (b) Relaxation rate versus metal content. The lower the metal content the faster the relaxation rate.

Figure 5. Electrical conductivity versus time as the SEM is vented. During the procedure first nitrogen enters the chamber. After approx. 6 min the door of the microscope slightly opens. 8 min later the door is fully open. The conductivity decreases with time at a rate which depends on the material composition. See text for details.
tent the faster the decrease. The reduction of the conductivity becomes faster at $t \approx 400\,\text{s}$, when the door of the chamber slightly opens and a small flux of air enters the microscope. At $t \approx 900\,\text{s}$ the door of the microscope is deliberately opened to fully expose the deposits to air. At this point the reduction rate of the conductivity strongly increases. According to figure 5, we divide the deposits into two groups exhibiting strong and weak degradation of the conductivity, respectively. To the first group belong samples #1, #2 and #5 with metal contents equal to 8.1, 8.9 and 15.6 at.%. After one hour from opening of the vacuum chamber the conductivity of these deposits has dropped to 7%–34% of its initial value. To the second group belong samples #6, #7 and #9 with 16.7, 31.5 and 38.7 at.%. In this case after one hour of exposure the value of the conductivity lies between 90% and 99% of the initial value. It is interesting to note that the degradation rate increases monotonically with decreasing metal content and, thus, with the beam power used to prepare the respective samples. Most likely the degradation is due to a reduction of the tunneling probability within the deposit. In the discussion section we speculate that the degradation rate can be linked to the density of the deposit which depends on the beam power [7].

3.4. Post-irradiation conductivity behavior

In order to study the effect of the beam irradiation on EBID deposits we consider two samples with W contents of 9 at.% (sample #3) and 14.7 at.% (sample #4), respectively. After preparation the samples were irradiated with the same electron beam power used during deposition, i.e. 5 nA keV and 10 nA keV, respectively. In figure 6(a) we plot the transient conductivity versus irradiation time. The conductivity of both samples abruptly increases during the first few seconds of irradiation. In the following minutes the conductivity increases monotonically at a much lower rate, which depends on the composition of the deposit. The conductivity of sample #3 increases to approximately eight times its initial value in 2000 s of irradiation. In the same time interval the conductivity of sample #4 increases only by 10% of its initial value. The increase of conductivity may be attributed to the increase of charge carriers released during the beam-induced breakage of carbon–carbon bonds in the amorphous matrix, as was speculated in [8, 9]. Sample #3 shows the largest increase of conductivity because it is the sample with the largest matrix volume fraction. In figure 6(b) we report the relaxation of the conductivity over a timescale of almost 3 days. The most remarkable fact is the very low decrease of the conductivity in comparison with its increase during post-irradiation. The second remarkable fact is that the conductivity is not logarithmically dependent on time. Therefore no relaxation of the conductivity takes place; rather, we suggest that the conductivity deteriorates because of exposure to the rest gases present in the SEM chamber. Note that in the frame of the ‘bond-breaking’ model we expect that carbon atoms bond again, leading to a conductivity decrease much faster than the one observed. Therefore we attribute the increasing conductivity during irradiation to a permanent chemical transformation of the deposit.

3.5. Temperature dependence of the electrical conductivity

In this section we present the temperature-dependent conductivity measurements performed for the samples with W content of 8.1 at.% (sample #1), 14.7 at.% (sample #4) and 31.8 at.% (sample #8). For the low conductivity samples #1 and #4 we choose an applied field between 1143 and 210 V cm$^{-1}$ in order to be able to measure $\sigma(T)$ down to the lowest temperature accessible in our set-up. In order to
avoid irreversible switching in the $I(V)$ characteristic during the measurements we used a current limit. For sample #8 we choose an applied field of 6.7 V cm$^{-1}$ in order to measure $\sigma(T)$ in the linear regime of the $I(V)$ characteristic. In figure 7(a) we plot the conductivity versus temperature dependence for samples #1 and #4. Both samples show the characteristics of systems governed by variable-range hopping, i.e. $\sigma = \sigma_0 \exp[-(T_0/T)^\alpha]$. In particular, we observed $\alpha = 0.39$ and $\alpha = 0.36$ for samples #1 and #4, respectively. In figure 7(b) we plot the temperature dependence of the electrical conductivity for sample #8. We find that the conductivity follows a modified power law over the complete temperature range of our measurement ($1.8 \, \text{K} \leq T \leq 265 \, \text{K}$) with $\sigma = \sigma_0 + aT^\beta$, with $\beta = 0.55$. Such a behavior is similar to the one recently reported in [14] and may indicate the onset of coherent tunneling contributions in the limit of large inter-grain coupling [14, 15].

4. Discussion

4.1. Time-dependent electrical conductivity and shell-growth mechanism

In general, a linear increase of the time-dependent conductivity can be explained by supposing a linear time-dependent growth of the thickness. However, the measurements performed during growth show an increase of the conductivity versus time faster than linear. Therefore, an additional mechanism which contributes to the enhancement of the conductivity has to be considered. Possible additional mechanisms for the increase of the conductivity growth rate include an enhancement of the electron carrier density and of the metal particles’ size during deposition, both due to the electron beam irradiation. In the following we relate the time dependence of the conductivity to the increase of the metal particles’ size by means of a ‘shell-growth’ model.

4.1.1. Shell-growth model. We consider a sphere of radius $r$ and volume $v_0$ representing a metal particle, see figure 8. A coordination sphere of radius $l$ and volume $v_l$ surrounds this spherical particle. The radius difference $s = l - r$ represents the separation between two neighboring particles. The ratio $v = v_l/v_0$ gives the metal–volume fraction of the system. It follows that the diameter of the metal particle is $d = 2r = 2v^\frac{1}{3}$. We suppose that at time $t = t_0$ the deposit is constituted by particles with the same radius $r$. The particles of this initial deposit increase their volume because of electron-beam-stimulated diffusion of W atoms. In general, the growth rate of the particle size is described by the Lifshitz–Slyozov coarsening law $r \sim t^n$ [16]. However, lower growth rates with $n > 3$ have also been reported [17, 18], which indicate diffusion-limited mass transport. Knowing the diameter $d$, the separation $s$ and the growth rate, the time dependence conductivity in the variable-range-hopping (VRH) regime can be deduced from equation (2) [19]:

$$\sigma \sim e^{-2s^2/k_BT}$$

with $\xi$ is the localization length, $k_B$ the Boltzmann constant, $T$ the temperature and $W$ the effective activation energy for charge transport [19, 20]. The time dependence of the conductivity is implicit in the localization length and in the activation energy, both dependent on the particle diameter. In particular, $\xi = \xi_{mx}(1 + d/s)$, with $\xi_{mx}$ being the localization length of the matrix [19]. The localization length

![Figure 7. Temperature dependence of the electrical conductivity. Left figure: the temperature dependence for samples characterized by variable-range hopping, $\sigma \propto \exp(-T_0/T)^\alpha$. The exponents $\alpha = 0.39$ and $\alpha = 0.36$ are found for samples with W contents of 8.1 at.% (sample #1) and 14.7 at.% (sample #4), respectively. Right figure: temperature dependence for sample #8 with W content of 31.8 at.%. The conductivity increases with temperature as $\sigma = \sigma_0 + aT^\beta$, with $\beta = 0.55$, $\sigma_0 = 5.27 \, \Omega^{-1} \, \text{cm}^{-1}$ and $a = 0.08 \, \Omega^{-1} \, \text{cm}^{-1} \, \text{K}^{-1}$.](image-url)
is obtained from the relation

\[ \xi_{\text{max}} = \frac{2.86^2}{4\pi \varepsilon_0 k_B T_0} (1 + d/s) \]

[21], where \( \varepsilon \) is the dielectric constant of the deposit and \( T_0 \) a constant deducible from the temperature-dependent conductivity measurements. From the experiments one also extracts the activation energy \( W = a k T (T_0 / T)^n \) [19]. From figure 7(a) it results \( T_0 = 1.28 \times 10^5 \) K and \( T_0 = 6.4 \times 10^3 \) K, for samples #1 and #4, respectively. The values of the dielectric constant necessary to calculate \( \xi_{\text{max}} \) are chosen considering that for a carbon matrix \( \varepsilon \approx 4 \) [22] and that with increasing metal volume fraction the dielectric constant of a metal–insulator composite increases [23]. By using for \( \varepsilon \) the values 8 and 12, it follows that \( \xi_{\text{max}} = 0.02 \) nm and \( \xi_{\text{max}} = 0.1 \) nm, \( \xi = 0.03 \) nm and \( \xi = 0.61 \) nm for samples #1 and #4, respectively. For a comparison, note that the value of the localization length of amorphous carbon thin films lies between 0.1 and 1.2 nm [24]. In figure 9 we report the time-dependent conductivity measurements during growth for samples #1 and #4. In order to fit the experimental data, we choose a linear increase of the metal volume fraction \( v \) from 0.04 to 0.06 and from 0.04 to 0.35 for samples #1 and #4, respectively. In table 2 we report the parameters used to obtain the best fit.

In conclusion, the experimental data on the growth process can be well described within our ‘shell-growth’ model by using a coarsening growth rate which depends on the deposit’s metal content and, thus, on the beam parameters. We find that in the deposit with lowest metal content (sample #1, \( n = 9.8 \)) the size of the metal particle increases in time at the lowest rate, as one may have expected. The coarsening law of Lifschitz–Slyozov is not reached by the range of beam parameters used for samples #1 and #4. We believe that, for higher deposition rates, such a regime may be reached.

It has to be noted that we cannot describe the behavior of sample #9 by means of the previous modeling because the parameters \( T_0 \) and \( \xi \) cannot be deduced from the temperature dependence of the conductivity of figure 7(b). However, it is quite possible that in the first stages of the deposition process the electron transport may be described by the VRH theory. In this case, the growth rate of the particle size of sample #9 shall be much higher than the one of samples #1 and #4, being close to the Lifschitz–Slyozov theory. Indeed, a hint that this may be the case is given by the different power law, which is \( \sigma^i = t^i \) for sample #9 in the first seconds of deposition, while it is \( \sigma^i = t^{1.86} \) for sample #1 during the whole range of deposition times. It is important to note that the ‘shell-growth’ model assumes the presence of nanocrystal particles in the deposit. According to the TEM measurements of Hoyle et al [5] this assumption is fully justified for deposits prepared with high doses. For deposits prepared with a dose per loop smaller than 500 C m\(^{-2}\) the authors of [5] found amorphous material. However, the presence of very small crystals not detectable from TEM measurements cannot be excluded. Indeed, the sharp fall of the conductivity with the decrease of the doses (see the inset in figure 2) may also be explained by the Coulomb blockade of small nanocrystals at room temperature.
If \( r^* < s \) the tunneling between localized states is not possible (sample #1). If \( r^* > s \) the tunneling between localized states is possible (sample #2).

### Table 3. Comparison between the typical hopping distance for electrons, \( r^* \), and the separation between neighboring particles, \( s \).

| Sample | \( r^* \) (nm) | \( s \) (nm) | Tunneling |
|--------|----------------|-------------|-----------|
| #1     | 0.46           | 0.55–0.59   | No        |
| #4     | 1.69           | 0.42–0.99   | Yes       |

#### 4.2. Electronic transport mechanism

In granular materials it is observed that in the low conductivity tunneling regime the temperature dependence of the electrical conductivity is of the form \( \sigma \sim \exp[-(T/\alpha)^\beta] \), with \( 0.25 \leq \alpha \leq 0.5 \). For our samples we find \( 0.36 \leq \alpha \leq 0.5 \) with metal content \( \leq 19\% \), which may indicate a tunneling mechanism either involving localized sites in the matrix or directly between the metal grains. However, in order to have tunneling the typical hopping distance for the electron

\[
r^* = \left( \frac{e^2 \xi}{4\pi \epsilon \epsilon_0 k_B T} \right)^{0.5}
\]

has to be larger than the distance \( s \) between the localized states [21]. For samples #1 and #4 we obtain at room temperature \( r^* = 0.46 \) nm and \( r^* = 1.69 \) nm, respectively.

By comparing these numbers with the ones for \( s \) given above by the ‘shell-growth’ model, see Table 3, we find that in our deposits direct tunneling between grains appears to be possible. On the other hand, tunneling between localized sites in the matrix is not favorable. However, this does not exclude conduction inside the matrix which may also take place between localized matrix sites bridged by metal grains. As a consequence, in the following we speculate that the transport mechanism in our deposits takes place by means of two channels: directly between grains and indirectly between localized sites in the matrix through a grain. In order to describe the transport mechanism we use the following formula:

\[
\sigma = a\sigma_{01} e^{-(\frac{2\mu}{\xi})^\beta} + b\sigma_{02} e^{-(\frac{2\mu}{\xi})^\beta} + \sigma_{03} e^{-(\frac{2\mu}{\xi})^\beta}.
\]

The first two terms of equation (4) take into account the tunneling of electrons between trap sites in the matrix [10, 11] and between grains [12, 13], respectively. The factor \( a \) gives the volume concentration of the matrix, while \( b \) refers to the concentration of the metal. The third term of the equation takes into account the hopping of electrons between trap sites and grains. The temperature \( T_{03} \) and factor \( \beta \) are free parameters. By fitting the experimental curves with equation (4), we obtain the volume concentration of the matrix and of the metal. We made the fit to the two curves of figure 7, for which we have \( W \) contents of 8.1 and 14.7 at.\%. In Table 4 we report the parameters used for the fit.

We can compute the fractional volume obtained by the fit with the one deduced by EDX measurements. The fractional volume occupied by the metal particles depends on the density of the metal and of the matrix, which is not well known. The lower and upper limit corresponding to a density of 1.8 g cm\(^{-3}\) (graphite-like amorphous) and 3.5 g cm\(^{-3}\) (diamond-like) lead, for the \( W \) content of 8.1 at.\%, to a fractional volume between 12 and 20 vol\% [14]. From our fit we obtain a volume of 6\%, which would indicate a lower density than a graphite-like matrix. This difference may be due to the presence of oxygen atoms inside the carbonaceous matrix. By means of in situ mass measurements the density of the matrix of \( W \)-based deposits from \( W(CO)_{6} \) has been related to the electron beam parameters used during deposition by Sawaya et al [7]. They found that the density of the matrix increases with the power of the electron beam. The authors measured a matrix density between 0.29 and 0.88 g cm\(^{-3}\), corresponding to a \( W \)-volume concentration between 11.1 and 6.4 vol\% [7, 25]. These results were obtained for beam voltages between 5 and 15 keV, but with a beam current much higher than the one used in our depositions. For a sample with \( W \) content of 14.7 at.\%, we calculate a fractional volume between 19 and 33 vol\% for graphite- and diamond-like matrix, respectively.

The value of 35 vol\% obtained within our modeling is close to that for a diamond-like matrix. Note, however, that the matrix of our deposit is non-crystalline and does also contain oxygen. In conclusion, we find clear evidence of an increase of the density of the matrix by increasing the electron beam power. This result is in accord with the one obtained for amorphous carbon deposits obtained by electron-beam-induced deposition [7, 25].

#### 4.3. Time-dependent relaxation of the conductivity

After terminating the growth process the conductivity starts to decrease with the logarithm of the time, see figure 4. The relaxation can be attributed to the migration of the charge carriers out of the sample. In general, in order to describe the relaxation of a system towards equilibrium a stretched exponential of the form \( \sigma \sim \exp[-(t/\tau)^\beta] \), with \( 0 \leq \beta \leq 1 \), can be used [26]. In the case of \( \beta = 1 \) Debye relaxation is obtained, which is valid for systems with weak dynamic correlations. In the case of hopping conductivity, this corresponds to a system with no Coulomb interactions. If the system presents strong dynamic interactions, the law of Kohlrausch [26] can be obtained by considering a serial relaxation of hierarchies of correlated systems [27]. In the case of hopping conductivity, this corresponds to a system with strong Coulomb interactions, dynamically described by the tunneling of an electron into a localized state, which is possible if a second electron tunnels into another localized state (co-tunneling). The logarithmic decay of the variable describing a system finds an explanation in the frame of hierarchically constrained dynamics [28]. In particular, in the theoretical study of [29] it is mentioned that the conductivity of systems governed by hopping conduction can exhibit a logarithmic time dependence, as we find experimentally. Finally, we observed an increase of the relaxation rate at lower \( W \) concentration. We attribute this behavior to the increased number of localized sites in the matrix and, therefore, to an higher probability for the electron to tunnel into a free localized state.
Figure 10. Decay of the conductivity during exposure to air. Left figure (a): the decay, as exemplarily shown for sample #7, is described by the sum of two exponential decay channels according to \( \sigma = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \). Each decay channel is associated with a tunneling mechanism: either between grains and trap sites in the matrix (decay constant \( \tau_1 \)) or between metal grains (decay constant \( \tau_2 \)). Right figure (b): ratio between the weight of the two tunneling mechanisms, \( a_1/a_2 \). For deposits prepared at small beam power the tunneling involving the matrix is dominant.

4.4. Time-dependent conductivity during air exposure and post-irradiation

The increase of the density of the matrix with the electron beam current (see above) can be used to interpret the conductivity measurements obtained during air exposure. The degradation rate is smaller as one considers deposits prepared at larger beam current (power) and, thus, having a larger density of the matrix. In order to better describe the degradation process, we fit the experimental data of figure 5 from the time when the door of the microscope is opened (\( t \approx 900 \) s) with a sum of two exponential functions:

\[
\sigma \propto a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2}.
\]

In figure 10(a) we plot a typical decay fitted with such a curve. In figure 10(c) we report the decay constants \( \tau_1 \) and \( \tau_2 \) for the deposit measurements depicted in figure 5 as a function of the beam power used to prepare the samples. Both decay constants increase with the beam power with (15 s \( \leq \tau_1 \leq 236 \) s) and (510 s \( \leq \tau_2 \leq 2185 \) s). As one observes from figure 10(b) the weight of the first term of the exponential sum is larger than the weight of the second one (\( a_1 > a_2 \)). In particular the ratio strongly increases for small values of the beam power, which corresponds to deposits mainly constituted by the matrix. Therefore we associate the first term of the exponential sum to the matrix. The decay constant \( \tau_1 \) is associated with the decrease of the tunneling probability within the matrix, or between the matrix and grains in view of our previous discussion. The increase of the decay constant \( \tau_1 \) with beam power is interpreted as due to the increase of the matrix density. The second term of the exponential sum may describe the decay of the tunneling probability between metal grains. The increase of the decay constant \( \tau_2 \) with beam power may be interpreted as due to the increase of the grain size.

Similar considerations are useful in order to analyze the behavior of the deposits after irradiation. Also in this case the conductivity can be described by the sum of two exponential functions. The two decays are independent processes linked to the decrease of the tunneling probability within the matrix and between the metal grains. The decay constants of sample #4 and sample #3 are \( \tau_1 = 1.91 \times 10^4 \) s, \( \tau_1 = 2.33 \times 10^4 \) s and \( \tau_2 = 1.66 \times 10^5 \) s, \( \tau_2 = 1.6 \times 10^5 \) s, respectively. These values are 2–3 orders of magnitude larger than those obtained by venting the system. The timescale is much longer because the residual pressure \((\approx 4 \times 10^{-6} \) mbar\)] inside the microscope is many orders of magnitude lower than in the environment. From the literature it is known that the presence of residual oxygen and water molecules inside an SEM is sufficient to oxidize W-based granular metals prepared from the tungsten hexafluoride (WF6) precursor [30]. Similarly, the oxidation of the deposits is most likely the reason for the observed decrease of the conductivity that we measured inside the SEM.
5. Conclusions

In this work we have shown that in situ conductivity measurements can be used to get a quite detailed insight into various aspects of the electron-beam-induced deposition process and the time evolution of the electronic properties of the deposits. Probably, the most relevant technological aspect concerning our study is the investigation of the behavior of W-based granular metals during exposure to air. We have found that the degradation of the system strongly depends on the composition. In particular, after one hour of exposure to air the remaining conductivity varies between 7% and 99% of its initial value for deposits with W contents in the range 8.1 at% ≤ W ≤ 38.7 at%. Transient electrical conductivity measurements indicate that this dependence is due to the different densities of the deposits. Furthermore, the decay of the conductivity involves the matrix and the W-metal grains on two different timescales. In view of the possible employment of EBID W-based deposits for applications, the composition of the composite has to be carefully chosen to minimize the aging effect. In this regard it is remarkable that, after one year from deposition, two samples with W contents of 34% and 19%, respectively, show a decrease of conductivity only of a factor between two and four. However, covering the deposit with a protective SiOx layer, for example, the tetraethylorthosilicate (TEOS) precursor may be necessary to prevent long timescale degradation of the electrical properties [3].

By means of transient electrical conductivity measurements we have monitored the growth process of W-based deposits. In order to explain the nonlinear growth of the conductivity versus time we have used a ‘shell model’ based on the hypothesis that the diameter of the W-metal particles grows during deposition. Within the modeling we have estimated the average particle size in the final deposit, which ranges between 0.71 and 2.16 nm for deposits with W contents of 8.1 and 14.7 at%. It would be interesting to extend this analysis with transmission electron microscopy investigations.

Furthermore, we have investigated the electrical transport mechanism as a function of the deposits’ composition by means of conductivity versus temperature measurements. From the analysis of the experimental data we have speculated that the electrical transport takes place by means of two parallel channels involving both the direct tunneling between metal particles and the indirect tunneling between localized sites in the matrix bridged by metal particles. As a consequence of this investigation information about the matrix density can be deduced, which is useful to interpret the data of the conductivity versus time we have used a ‘shell model’ based on the hypothesis that the diameter of the W-metal particles grows during deposition. Within the modeling we have estimated the average particle size in the final deposit, which ranges between 0.71 and 2.16 nm for deposits with W contents of 8.1 and 14.7 at%. It would be interesting to extend this analysis with transmission electron microscopy investigations.

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