Ruthenium Electrodeposition from Deep Eutectic Solvents

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Ruthenium is electrodeposited for the first time from a deep eutectic solvent based electrolyte composed of ethylene glycol and choline chloride in 1:2 molar ratio. Deposition is found to effectively occur upon addition of sulfamic acid to the Ru(III) containing deep eutectic solvent. The main consequence of the presence of sulfamic acid, as evidenced by the electrochemical characterization performed, is the oxidation of Ru(III) to Ru(IV). Consequently, Ru electrodeposition is demonstrated to take place from the tetravalent state. Optimized plating conditions are able to yield uniform and crack-free Ru coatings up to 0.8 mm thickness. No oxides or other notable secondary phases can be individuated in the obtained metallic layers. Morphological and electrical properties of the layers obtained are comparable with Ru coatings deposited from sputtering and suggest possible applications in the electronics field as barrier layers for interdiffusion.

The aim of the present paper is the investigation of ruthenium electrodeposition from a DES obtained mixing choline chloride and ethylene glycol in 1:2 molar ratio. This DES, belonging to the class III and commercially known as ethaline, is characterized by interesting physical and chemical properties and it constitutes a good electrolyte for the deposition of many metals. Deposition is optimized and resulting coatings are characterized to exclude the possible presence of oxides or other secondary phases. Moreover, the possible application of Ru electrodeposition from DESs for barrier layers manufacturing is investigated by depositing Ru on seeded silicon wafers.

### Experimental

All the chemicals used during the experimentation were acquired from Sigma Aldrich. Most of such chemicals were used as received, except RuCl₃ · nH₂O, RuCl₃ · nH₂O was dried according to a procedure available in literature to limit the presence of oxo- or hydroxo-chloro complexes and nitrosyl species. The material was initially dried for 3 h at 120 °C. During this first step, ruthenium chloride lost significant quantities of water. The resulting mass was then ground in a mortar and again heated at 120 °C for 1 h. Anhydrous RuCl₃ was then stored in a desiccator to avoid moisture adsorption. Choline chloride (ChCl) was mixed with ethylene glycol (EG) in a 1:2 molar ratio to obtain the base DES electrolyte. RuCl₃ in different amounts (20 or 40 mM) was then added to form the plating solution, which
was stirred for 12 h to completely homogenize. Where used, sulfamic acid (SA) was added in variable amounts and the solution was stirred for 12 h to completely homogenize. All plating baths were employed at 80°C. Plating parameters are detailed in the results and discussion part. Where employed, agitation was provided using magnetic stirring. Cu sheets and Au (120 nm thickness) sputtered on ultraflat Si wafers were used as substrates after cleaning with acetone. Cu oxide was removed immersing Cu substrates in a 5% HNO3 solution for 1 min. Cathodic efficiency was evaluated by calculating the amount of deposited material from the thickness of the coatings. Electrolytes conductivity was measured employing a parallel Pt plates Amel 160 conductivimeter. Cyclic voltammetry (CV) was performed on the solutions using glassy carbon as working electrode, a Pt wire as reference and graphite as counter. All the voltammetric tests were performed using an AMEL 2550 galvanostat/potentiostat. Pt is widely recognized as quasi-reference electrode and it was employed in this case due to the high temperature of the solution and to its significant Cl− content (which may damage normal commercial reference electrodes). Potential was ranged between +2 and −3 V during the CV tests and no stirring was employed. Ru thickness was measured using a XRF X-RAY XAN apparatus by Fischerscope. AFM was performed employing a NT-MDT SOLVER PRO (in tapping mode). SEM characterization, a Zeiss EVO 50 EP was used. Such SEM setup was equipped with an energy dispersive X-ray analyzer (EDS) Model 7060 from Oxford Instruments. XRD analysis was performed using a Philips Xpert MPD in thin films configuration with Cu Ka = 1.5406 Å. UV-VIS spectroscopy was carried out using a Jasco V570 spectrometer. Glow discharge optical emission spectroscopy (GDOES) was performed using a Model GDA 750 analyzer by Spectrum Analytic GmbH. To obtain the substrates used for electrical characterization, 10 nm of Ru were sputtered on ultraflat Si wafers. Ru/Si substrates were immersed, before Ru deposition, in a 10 g/l sulfamic acid solution to remove any oxide layer present on the surface. Finally, sheet resistance of films deposited on Si was measured by mean of a linear 4 points probe setup.

Results and Discussion

Ru deposition optimization.—Initially, galvanostatic ruthenium electrodeposition was attempted from a mixture of ChCl/EG and 40 mM RuCl3. Copper was used as substrate and current density was varied over a broad range, but no reproducible ruthenium plating was achieved. It was observed, in particular, that Ru deposition took place in an unpredictable way, with some batches of the same bath depositing Ru at extremely low current efficiencies and some others depositing no Ru at all. In the cases where electrodeposition took place, the copper substrate was covered irregularly with gray areas. It was however not possible to achieve efficient and reproducible ruthenium deposition in the conditions described. The chemistry of the plating bath was therefore modified in an attempt to obtain stable Ru deposition. According to existing literature, Ru deposition in ILs like BMIM based electrolytes has, as necessary prerequisite, the formation of Ru(IV) complexes. Moreover, aqueous Ru plating takes place from a Ru(IV) complex (the μ-nitridobisaquatetrachlororuthenate).

For these reasons, the possibility to use an acid to oxidize Ru(III) to Ru(IV) was examined. In particular, sulfamic acid (SA) was used in variable amounts. This acid is a typical component of aqueous Ru plating solutions, as it is necessary to form the bridged nitride complex. SA was therefore employed also for the DES electrolyte. Figure 1a clearly shows the effect of different sulfamic acid additions to a 40 mM RuCl3 solution in ChCl/EG. No stirring was used...
to acquire the data presented in Figure 1a and the current used for deposition was kept constant at 10 mA/cm². It can be noticed that, exceeding a threshold concentration of about 80 mM, addition of SA triggered Ru deposition. Further increase of SA concentration improved plating speed and efficiency, up to a maximum at 800 mM SA. After this concentration, it became difficult to completely dissolve SA in the DES. For this reason, deposition speed reached a plateau after 800 mM. Accordingly, 800 mM SA was selected as optimal concentration for the following experiments presented in the paper. Oxidation of Ru(III) to Ru(IV) and potential formation of Ru(IV) bridged complexes analogous to the one observed in water can be possible reasons for the deposition of Ru only after addition of sulfamic acid to the bath. To perform a first validation of these two options, the same procedure was repeated using sulfuric acid (SU) in place of SA. Sulfuric acid is a strong oxidant, but lacks the nitrogen moiety necessary to form the bridge between the two ruthenium atoms in the μ-nitridobisquatercatrachlororuthenate complex. As visible in Figure 1a, also SU triggered Ru deposition after a threshold concentration in a way similar to SA. This result constitutes a first evidence that the formation of the bridged complex is not at the base of Ru deposition in the DES and it suggests that the oxidizing action of the acid added to the bath is the key factor to achieve reproducible deposition. The two acids produce similar effects on the chemistry of the plating bath, oxidizing Ru(III) to Ru(IV).

Since RuCl₃ solubility in the DES is considerably low, only concentrations up to 40–50 mM can be achieved. Under these conditions, considering also the comparatively high viscosity of the ChCl/EG DES, deposition is strongly limited by the concentration of ruthenium ions present in the solution. Figure 1c shows the effect of progressive SA additions on two solutions containing 40 and 20 mM RuCl₃ respectively. In both cases, Ru deposition took place at high enough SA concentrations, but deposition rates were significantly different. The solution containing less ruthenium trichloride was characterized by lower plating rates, compatible with the comparatively low concentration of ruthenium ions. Deposition was attempted from the 40 mM RuCl₃ solution, which maximizes the growth rate. Ru layers obtained at 10 mA/cm² and 30 min of deposition on copper without stirring were characterized by a uniform appearance and a gray color. Their microstructure, visible in Figure 1b at the SEM, was fine grained and crack-free. Thickness was found to be around 380 nm. Deposition was attempted also on gold (120 nm sputtered on ultraflat Si wafers) at 10 mA/cm². In this case, precipitation of polygonal crystals on the surface was found to occur. Figure 1d depicts the typical appearance of a Ru layer plated on Au in the same conditions as the sample visible in Figure 1b. In this case, the use of stirring was attempted (300 rpm). However, crystal precipitation was found to occur both with and without stirring. The holes visible in Figure 1d are not due to delamination of the Ru layer, since there are no cracks or residues at the edges of the imperfections. Their formation takes place during deposition, with the precipitation of polygonal crystals on the surface of the electrode. Ru cannot grow where there are such crystals and, for this reason, water washing at the end of deposition can remove the crystals and can leave the polygonal holes visible in Figure 1d. Ru growth was observed also on the bottom of some of these imperfections. Indeed, if a crystal is released from the surface during deposition, Ru can grow inside the space left by the crystal itself. The depth of the holes present on the surface was evaluated via AFM to be between 450 and 500 nm, value that corresponds to the thickness of the coating (480 nm). The presence of precipitates during Ru deposition in ILs has already been reported in the case of BMIM containing electrolytes. It was hypothesized, for BMIM based baths, that compounds of the type RuₓX₃₋ₓYₓ (X = NTF₂ or PF₆, Y = Cl and x can be 0–3) are responsible of the phenomenon, which takes place at concentrations higher than 15 mM Ru(III) in BMIMNTF₂ and 40 mM Ru(III) in BMIMPF₆. In the case of ChCl/EG, it seems that a similar phenomenon takes place. Crystals precipitation on the surface depends however on the substrate, since no crystals were observed in the case of deposition on Cu. It is possible that only some substrates catalyze crystal formation, indicating the presence of an electrochemical mediated precipitation mechanism.

Electrolytes characterization.—The Ru containing electrolyte was characterized from the electrochemical point of view by performing conductivity measures and voltammetric studies. Figure 3a describes the correlation between conductivity and temperature for

![Figure 2. Stirring vs. grow rate relationship at 10 mA/cm² (a); current density vs. grow rate relationship at constant stirring rate (300 rpm) and 20 mM RuCl₃ + 800 mM SA (b).](image-url)
the ChCl/EG DES, DES + 20 mM Ru and DES + 20 mM Ru + 800 mM SA. Pure DES presents values of conductivity typical of 1:2 molar mixtures of ChCl and EG. Addition of 20 mM RuCl₃ slightly improves conductivity, as expected from the addition of metallic ions with high mobility to the DES, which is in turn characterized by low ionic mobility and conductivity. Conversely, the presence of SA together with RuCl₃, results in values of conductivity analogous to the pure DES. This indicates that SA poorly dissociates in the electrolyte.

Voltammetric tests were performed to understand Ru deposition mechanism from ChCl/EG. ChCl/EG, in accordance to existing literature, presents an electrochemical window of −2/+1.1 V vs. Pt, compatible with the electrodeposition of many metals. Addition of SA was found to strongly narrow the potential window on the cathodic side of the voltammetric diagram (Figure 3b), with parasitic reactions starting at a potential around −1200 mV vs. Pt. When RuCl₃ was added to the electrolyte, the appearance of two distinct features was observed. The first one, marked with Ru₃ in Figure 3b, was found to start around −750 mV and presented a peak at −1000 mV. Ru₃ was associated with reduction of the Ru³⁺ ions present in the solution. The second feature, marked with Ru₄ in Figure 3b, presented a peak at −1200 mV. Such peak was associated with reduction of Ru⁴⁺ ions. It was reported that commercial RuCl₃ contains, as a consequence of natural oxidation, Ru(IV) species. Furthermore, the heat-treatment performed on the RuCl₃ probably slightly changed the ratio Ru³⁺/Ru⁴⁺ in favor of the Ru(IV) moieties. For these reasons, it is somewhat expected to observe both Ru³⁺ and Ru⁴⁺ reduction from the voltammetry performed. If SA (800 mM) was present in the solution together with RuCl₃, Ru₃ was not observed anymore. As evident from Figure 3b, only Ru₄ is visible in the voltammetry of the 40 mM RuCl₃ + 800 mM SA solution. In this case, Ru₄ peak was found at −1200 mV, while the beginning of the reduction process was individuated around −900 mV. It can be observed from Figure 3b that in the presence of RuCl₃ alone, the limiting current at potentials over −1500 mV roughly corresponds to the one of DES + SA. Conversely, when RuCl₃ and SA are present at the same time, limiting current is comparatively higher. In accordance with what observed during the electrodeposition experiments performed in Ru³⁺ containing DES, no metallic Ru deposition was observed in correspondence of the onset potential of Ru₃ (−750 mV vs. Pt). Conversely, Ru deposition was observed in correspondence of the onset potential of Ru₄ (−900 mV vs. Pt). Considering this, and due to the presence of a single cathodic feature (Ru₄) in Ru(IV) containing solution, it is reasonable to infer that Ru ions directly reduce to metallic Ru from the tetravalent state, according to expression (1):

\[
\text{Ru}^{4+} + 4e^- \rightarrow \text{Ru}^0
\]

Conversely, the trivalent state is unable to provide metallic Ru deposition. A possible reason for this phenomenon is the formation of
very stable complexes with chloride ions, as already observed in the case of BMIM chloride based ILs by Jayakumar et al. Ru4 peak can therefore be associated to the electrodeposition of such Ru(III) complexes to valence states higher than 0. In this context, the redox couple Ru(III)/Ru(n), with n > 0, presents a potential higher than the Ru(IV)/Ru(0) couple. Finally, a peculiar feature (RuP) was observed in the case of the RuCl3 + SA solution. This peak was associated with the electroprecipitation of chloride containing compounds on the surface of the electrode, which may be at the base of the morphology observed in Figure 1d. No significant anodic peaks were individuated both in presence and absence of SA in correspondence of the cathodic features observed, indicating a strong irreversibility of the electroreduction process. The anodic feature visible around +250 mV vs. Pt in Figure 3b was observed only in the case of the RuCl3 containing electrolyte, without SA. Such peak can be associated to the possible oxidation of the Ru(III) chloride complexes previously hypothesized.

Figure 4a shows the effect of RuCl3 concentration on the voltammetry. It is evident from the graph that RuP disappears in the case of the 20 mM RuCl3 electrolyte, while Ru4 is always present. It is fundamental to notice that no crystals precipitation was observed at 20 mM RuCl3. The lack of the RuP peak in the 20 mM RuCl3 graph constitutes a reasonable evidence of its connection with chloride containing species precipitation. Figure 4b depicts the effect of scan speed on the voltammetries performed on the DES + 800 mM SA + 20 mM RuCl3 solution. As expected, the cathodic peak associated to Ru4+ reduction slightly moves to more negative potentials by increasing scan speed. Moreover, its intensity increases.

Figure 5a shows a voltammetry analogous to the one depicted in Figure 4a for the DES + 800 mM SA + 20 mM RuCl3 solution. In this case, however, a second cycle was performed. It can be immediately seen that, during the second cycle, two new peaks appear (Ru2 and Ru3). Ru3, as previously said, can be associated with Ru3+ reduction, while Ru2 can be attributed to Ru2+ reduction. The reason for this behavior is described in Figure 5b. During the first cycle, Ru4+ is the only reducible specie. For this reason, when the GC electrode works as cathode, only the single Ru4+ reduction peak can be observed (Figure 5b). As the analysis proceeds, the GC electrode continue working as cathode and Ru4+ is reduced to Ru3+, Ru2+ and Ru0. The two (II) and (I) valent ions stay in close proximity of the GC electrode due to the lack of stirring and to the high viscosity of the DES. When the GC works as anode, no significant reactions take place due to the strong irreversibility of the system. During the second cycle, when the GC again works as cathode, Ru2+ and Ru3+ ions are reduced (Figure 5b). This yields the two peaks Ru2 and Ru3. Presence of Ru2+ can be easily inferred from the color of the electrolyte in close proximity of the GC surface. When the electrode is removed from the solution at the end of the test, the DES present on the surface appears green. Ru2+ ions are reported to be blue. When blue is combined with the yellowish-brown tinge of the Ru4+ containing solution (insert of Figure 6), the final result is a green color. The behavior observed constitutes another evidence to support the presence of Ru in the (IV) valence state in the electrolyte.

The most evident effect induced by the presence of SA on the RuCl3 solution is the change in color, which strictly correlates with the electronic properties of the species present in solution. The inset presented in Figure 6 visually describes the phenomenon, while the UV-VIS spectra depicted in the same image quantify the alterations of the electronic transitions. Prepared electrolytes (ChCl/EG + 800 mM SA, ChCl/EG + 20 mM RuCl3 and ChCl/EG + 800 mM SA + 20 mM RuCl3) were diluted with the pure DES to avoid saturation of the absorbance signal. ChCl + 800 mM SA was diluted 1:4 vol., resulting in a concentration of 200 mM SA. ChCl/EG + 20 mM RuCl3 was diluted 1:100 vol., resulting in a concentration of 0.2 mM RuCl3. Finally, ChCl/EG + 800 mM SA + 20 mM RuCl3...
was diluted 1:50 vol., resulting in a concentration of 0.4 mM RuCl₃ and 16 mM SA. Pure ChCl/EG and ChCl/EG + SA does not present significant UV-VIS peaks. The same two solutions, additivated with RuCl₃, present three distinct peaks. Such three features, namely A, B and C in Figure 6, seem to be present for both solutions, either containing SA or not. Peak A was observed at 345 nm, peak B around 390 nm and peak C at 448 nm. Peak assignation is not immediate, since all the literature available describes the Ru electronic transitions taking place in aqueous environment.¹⁸ The usage of ChCl/EG in place of water as electrolyte is however expected to strongly alter the position of UV-VIS peaks due to the substitution of H₂O ligands with chloride ions around Ru within the coordination shell. For this reason, comparison with equivalent water electrolytes is difficult. Some considerations can be however done by correlating the UV-VIS peaks with the composition of the solutions analyzed. First, the presence of a bridged complex similar to μ-nitridobis(aqua)tetra(chlororuthenate) can be excluded. Campbell et al.⁴¹ report the main electronic transitions of [Ru₂(μ-N)(H₂O)₂Cl₈]³⁻ in the 360–400 nm range and around 300 nm. None of these peaks can be associated with the features visible in the DES + RuCl₃ case, because no SA is present in the solution and thus no bridged complex can form. Also in the case of the DES + SA + RuCl₃ solution the peaks cannot be directly associated. Formation of the bridged complex is expected to strongly vary the position of the electronic transitions. In the case of DES + SA + RuCl₃, however, the position of A, B and C looks identical to DES + RuCl₃. For this reason, formation of a RuNRu bridged complex can be excluded. Other information can be extrapolated from the height of the peaks. As previously said, commercial RuCl₃ is strongly contaminated by Ru(IV) species.¹⁸,³⁶ It is therefore reasonable to state that the UV-VIS spectra visible in Figure 6 for the DES + RuCl₃ solution is the result of the electronic excitation of both Ru³⁺ and Ru⁴⁺ containing species. After addition of SA, peak A intensity increases, while peak B and C intensity decreases. Since peak intensity can be correlated to the concentration of a particular specie by Lambert-Beer law, it can be reasonably stated that peak A is correlated to a moiey whose concentration increases by adding SA to DES + RuCl₃. As demonstrated by the electrochemical behavior of the solution, such specie can be Ru⁴⁺ ions. Accordingly, the remaining peaks intensity decrease due to conversion of Ru³⁺ to Ru⁴⁺. Deposition of Ru in ChCl/EG requires therefore the formation of Ru⁴⁺, in a way similar to what observed in the case of other ILs.

**Ru layers characterization.** — Ru layers obtained from the optimized electrolyte, containing 800 mM SA and 20 mM RuCl₃, were characterized from the morphological and microstructural point of view. Initially, the effect of plating current on the surface morphology was investigated. Figures 7a, 7b and 7c represent the SEM morphology of Ru deposits obtained at 5, 10 and 20 mA/cm² respectively on Au/Si. A constant total charge of 27 C was employed for deposition, resulting in plating times of 90 min (5 mA/cm²), 45 min (10 mA/cm²) and 22 min 30 s (20 mA/cm²). Resulting thicknesses, which were employed to calculate CE in Figure 2b, were as follows: 470 nm (5 mA/cm²), 340 nm (10 mA/cm²) and 200 nm (20 mA/cm²). It can be observed that the coatings are always crack-free, with a microstructure that progressively refines moving from low to high currents (compatibly with the uneven thicknesses). Nodules can be observed on the surface for all the deposits. EDS point analysis performed on such nodules evidenced that they are mainly composed of Ru, excluding thus precipitation of species (similarly to what observed in the case of other ILs).
in all cases. Ru deposition from the DES + SA + RuCl₃ solution can be performed not only galvanostatically but also potentiostatically. As an example, Ru was deposited for 60 min at −1000 mV vs. Pt on Au/Si. Final thickness was 210 nm, with the microstructure visible in Figure 7d. If the sample is compared with Figure 7c (Ru obtained at 20 mA/cm² presenting a similar thickness), it can be immediately noticed that the structure is highly nanocrystalline and the surface is considerably smoother. Also in this case, however, metallic nodules were present on the surface. It was observed that crack-free layers can be obtained up to 800 nm and more. Figure 7e reports the AFM analysis of a Ru coating deposited at 10 mA/cm², 300 rpm and 90 min as plating time. Thickness in this case is considerably high, 790 nm. However, no cracks can be observed on the surface. Average roughness Rₐ was measured from the AFM analysis, resulting in a value of 33 nm (on the 50 μm × 50 μm area showed in Figure 7e). Such value is relatively low if compared with the Rₐ of the uncoated Au/Si substrate (∼3 nm).

Ru layers were analyzed also to assess their purity and lack of organic contamination. Figure 8a shows the results obtained from XRD performed on a sample deposited on Au/Si. Only peaks related to phase pure metallic hcp Ru (JCPDS card 6-663) were observed during the analysis. The relatively high peak broadening observed in Figure 8a indicates a nanocrystalline structure. No peaks were observed for ruthenium oxides, whose absence was confirmed also by the extremely low intensity of the EDS oxygen peak observed. GDOES was performed as well on Ru plated on Au/Si. In this case, considering the reduced thickness of the Ru coating, a layer of copper was deposited on top to protect the surface from the initial plasma ignition (which may damage the Ru layer). A 1 μm thick copper layer was therefore electrodeposited using a commercial acidic solution. After this step, the sample was inserted in the GDOES instrument. As noticeable from Figure 8b, the Ru layer signal is clearly observable between the Au layer and the Cu protective coating applied on the surface. Negligible oxygen contamination was observed via GDOES, confirming thus the purity of the Ru layer deposited.

Ruthenium, as stated in the introductory part, can be proficiently used as barrier layer in ICs interconnects. Considering this possible application, Ru layers obtained from ChCl/EG were investigated from the electrical point of view to determine their sheet resistance. Ru was deposited on a Ru seed layer obtained by evaporation on Si. Figure 9a depicts the cross section of a Ru layer deposited on Ru/Si. Total thickness is 210 nm, resulting from 10 nm of sputtered Ru and 200 nm of electrodeposited Ru. Uniformity and adherence of the Ru coating are evident observing the morphology of the section. Figure 9b reports the values of sheet resistance obtained for different thicknesses of electrodeposited Ru. Values of thickness reported in Figure 9b does not refer to the total thickness of Ru (sputtered + electrodeposited), but only to the partial thickness of electrodeposited Ru. For this reason, the sheet resistance value at 0 nm of deposited Ru corresponds to the sheet resistance of the sputtered Ru layer. It can be observed that, as expectable, sheet resistance decreases with increasing Ru thickness. Values of sheet resistance are compatible with existing literature for barrier layers deposited from sputtering. This demonstrates that the
Ru layers obtained by deposition from the DES based electrolyte described in the present work have electrical properties comparable with Ru coatings obtained with more expensive and less flexible technique like sputtering. In this context, by comparing sheet resistance values, it can be reasonably supposed that Ru layers deposited from ChCl/EG meet the general requirements for barrier layer.43

Conclusions

Metallic Ru was successfully deposited for the first time from a choline chloride based deep eutectic solvent. Addition of sulfamic acid to the Ru(II) containing DES was found to trigger significant Ru electrodeposition, whereas the sulfamic acid free bath was unable to provide satisfactory plating. The main reason for this behavior, as evidenced by the electrochemical characterization performed on the electrolytes, was found in the oxidation of Ru(III) to Ru(IV). At concentrations of 20 mM for RuCl3 and 800 mM for SA, Ru(IV) electrodeposition was observed at potentials lower than −900 mV vs. Pt. Both galvanostatic and potentiostatic deposition from the same electrolyte yielded smooth and uniform Ru layers on Au and Cu. Galvanostatically plated Ru coatings were found to be free from oxides and cracks up to a thickness around 800 nm. The same coatings showed interesting electrical properties, analogous to layers obtained with more costly and less scalable techniques like sputtering. Ru electrodeposited from DES can therefore constitute, due to these favorable properties, an interesting material for interdiffusion barrier layers.

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