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ORIGINAL PAPER

The oxide electrochemistry of ruthenium and its relevance to trench liner applications in damascene copper plating

L. D. Burke · N. S. Naser · R. Sharna

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Abstract There is considerable interest in the use of ruthenium as an ultrathin trench liner in damascene copper plating used to fabricate on-chip interconnects. The problem is that when freshly deposited ruthenium films are exposed to air, their surfaces tend to undergo spontaneous oxidation, and such deposits (as demonstrated here) are reluctant to undergo reduction. Copper deposition in an acid plating bath occurs readily on the oxidized ruthenium, but the presence of oxide is known to have a detrimental effect both on the copper superfilling process and copper adhesion at the Ru/Cu interface.

Keywords Electrodeposition · Copper · Ruthenium · Trench liner · Interconnects

1 Introduction

There is considerable interest at the present time [1–13] in the possible use of ruthenium as an ultrathin trench liner in damascene copper plating which is currently employed in the microelectronics area for the production of on-chip interconnects. The advantages of ruthenium as a trench liner are that ideally it prevents copper transport from the filled trench into the silicon (thus averting device degradation), it is directly platable (dispensing with the need for a seed layer) and it provides strong adhesion between the electrodeposited copper and the barrier film (which reduces copper electromigration at the Ru/Cu interface). One of the problems with ruthenium is that the metal is susceptible to oxidation in air and aerated water [7, 9, 12] so that copper may be plated on to an oxide [2] rather than the metal barrier film. Some authors [2] have suggested that ruthenium oxidation is an advantage in that the oxide plugs the grain boundary diffusion passageways and thus maximizes the diffusion barrier performance of the ruthenium liner. However, Moffat and coworkers [9] claimed that such oxidation blocks underpotential deposition of copper and the adsorption of bath additives; they also pointed out that residual oxide results in weak Cu/Ru adhesion, low nucleation density and poor trench filling.

The main topic of interest in the present work is the oxide electrochemistry of ruthenium. This is more complex than is generally realized because, as discussed recently for gold [14] and copper [15], there are two limiting states for the metal surface (the low energy Equilibrated Metal Surface (EMS) and the high energy Metastable Metal Surface (MMS) state) and two limiting types of oxides (anhydrous, or α, and hydrous, or β, deposits). According to Pourbaix [16] Ru appears to be a very noble metal; according to his thermodynamic data [16] Ru is unoxidizable in acid solution below ca. 0.74 V (SHE) or 0.10 V (SMSE). However, Pourbaix's data relates to equilibrate bulk states and is a poor guide to behaviour when MMS states are involved, e.g.

(i) RuO_2 films (on Ti) are quite promising candidates for use as cathodes [17–20] for hydrogen gas evolution, at $E < 0.0$ V (RHE), in water electrolysis cells. Such unexpected behaviour (which has also been observed with IrO_2 films [21]) was attributed [20] to the hydration (or hydroxylation) of the outer layer of the oxide film whose reduction is strongly inhibited due to the intervention of a high-energy state of the metal, i.e. discrete Ru atoms or clusters of same. Such behaviour is reported here for hydrous (as opposed to thermally prepared, anhydrous [20]) ruthenium oxide deposits.

L. D. Burke (✉) · N. S. Naser · R. Sharna
Chemistry Department, University College Cork, Cork, Ireland
e-mail: l.d.burke@ucc.ie

(ii) As discussed earlier for gold [14] and platinum [22], metal surfaces which have a high coverage of MMS states (and freshly deposited Ru films may often be in this form) tend to undergo oxidation at unusually low potentials. It is evident that with Ru surfaces, in general, there is no clear separation in cyclic voltammetry responses between the adsorbed hydrogen, double layer and monolayer oxide behaviour. In his review of chemisorption at noble metal electrodes, Woods [23] did not describe any electrochemical method for measuring the surface area of Ru. However, in a subsequent publication, Woods and coworkers [24] pointed out that the charge, $Q_{H,S}$, for saturated hydrogen coverage cannot be measured for Ru but, instead, recommended a procedure based on the measurement of the charge, $Q_{O,C}$, associated with monolayer oxide reduction. It is evident from their work that the voltammetric response for ruthenium in acid is influenced by electrode pretreatment and (for electrodeposited Ru) by electrode age (see Figs. 1 and 3 in [24]). Conway and coworkers [25, 26] pointed out that a bulk Ru electrode, on cycling at a slow sweep rate (20 mV s^{-1}) in acid solution, yielded an unstructured CV response, the regions for oxide formation/reduction and hydrogen adsorption/desorption overlapping (the unstructured character of the response was attributed later by Conway and coworkers [27] to redox transitions in a film where interaction between the reduced and oxidized form of the Ru oxycations in the surface layer results in a marked broadening of the transition potential range). A degree of resolution of these two regions was achieved [25, 26] but only with electrodeposited Ru black electrodes; bulk Ru electrodes did not exhibit well-resolved adsorbed hydrogen behaviour. Later work [28] suggested that electrodeposited Ru is atypical as it contains a significant amount (ca. 50%) of physically adsorbed and chemisorbed water.

The main point stressed here is that the surface electrochemistry of ruthenium is more complex than that for instance of platinum and is not easily rationalized in terms of Pourbaix's E^0 data [16]. The metal has quite a strong affinity for oxygen species and its oxidation is likely to be enhanced due to the involvement of MMS states (the presence of the latter on freshly deposited Ru surfaces is favoured by the limited surface mobility of Ru [9]). A further major source of complexity is the reluctance of surface oxyruthenium species to undergo reduction in aqueous media.

2 Experimental details

Experiments were carried out using a Metrohm, type EA 876-20, cell which contained both the working and counter electrodes. The reference electrode, either reversible hydrogen in the same solution or (for copper plating work) a saturated mercury/mercury (I) sulphate electrode (SMSE, $E^{o}_{298K} = 0.641$ (SHE)), was contained in a separate vessel which was connected to the main cell using glass tubing; the narrow tip of the latter was placed close to the surface of the working electrode, i.e. it functioned as a Luggin capillary. The cell was usually operated at ambient temperature, ca. 20 °C.

Two types of Ru metal electrodes were employed: one consisted of a small Ru bar, 2 × 2 × 25 mm, supplied by Goodfellow; one end was soldered to a copper lead and the bar was then sealed, using Araldite, into a length of glass tubing leaving ca. 4 mm of the metal exposed. The second type consisted of an electrodeposited Ru film; a gold wire (1.0 mm diam, ca. 2.1 cm exposed length, sealed directly into soda glass) was immersed in 100 ml of 0.1 mol dm^{-3} HCl solution, containing 1 g of $RuCl_3 \cdot nH_2O$, and cathodized at 20 mA cm^{-2} for 1 min; the resulting deposit of microcrystalline Ru was washed with doubly distilled water before use. Two types of Ru oxide electrodes were also employed; one consisted of a Ti-supported, thermally prepared (and thus virtually anhydrous) RuO_2 deposit; details of the preparation, mode of operation, surface hydration and remarkable resistance to cathodic reduction of such deposits were described recently [20]. The second type of oxide deposit consisted of Ti-supported hydrous (or hydrated) RuO_2 produced by a procedure described by Hu and Huang [29]. A Ti wire electrode (1.0 mm diam, ca. 2.0 cm exposed length, sealed directly into soda glass) was degreased with acetone, etched for 10 min in aqua regia at ca. 40 °C and washed with doubly distilled water. It was then repetitively cycled in a solution of ca. 5×10^{-3} mol dm^{-3} $RuCl_3 \cdot nH_2O$ in 0.01 mol dm^{-3} HCl + 0.1 mol dm^{-3} KCl (pH ≈ 2.0) in a triangular manner between −0.1 and −1.0 V (SCE) at 50 mV s^{-1} for 120 cycles. The deposition of a charge storage active, hydrous Ru oxide deposit resulted in a substantial increase in the current response in CVs recorded during the latter cycling procedure (such responses are not shown here).

Most of the work described here involved cyclic voltammetry which was usually carried out with a computerized electrochemical workstation (CH Instruments, model 660 B). Typical copper plating conditions relevant to this work were described recently [15].

3 Results and discussion

3.1 The reluctance of Ru oxide species to undergo reduction

Thermally prepared RuO_2 electrodes are remarkably reluctant to undergo reduction [20], despite the fact that the outer regions of such oxide deposits undergo hydration [30] and are thus quite reactive, under hydrogen gas evolution conditions. Similar behaviour was observed here for hydrous, electrodeposited Ru oxide coatings on Ti. Typical CV responses for such electrodes are shown (as a function of upper limit, part (a), and sweep rate, part (b)) for acid (Fig. 1) and base (Fig. 2). In both cases a broad, quasi-reversible, redox response was observed, the main charge storage peak being attributed to a Ru(III)/Ru(IV) transition. The potential for the onset of hydrogen gas evolution, 0.0 V (RHE), was estimated to be ca. −0.70 V (SMSE) in acid (pH = 1) and ca. −1.45 V (SMSE) in base (pH = 13.5). The peaks involved were quite broad which may reflect either the heterogeneous character of the species involved in the hydrous oxide layer or, as pointed out by Conway and coworkers [27], appreciable interaction between the oxidized and reduced oxyruthenium species. Unlike some of the other noble metals, e.g. iridium and rhodium [31], the charge storage reaction of the hydrous ruthenium oxide layer is not accompanied by an electrochromic effect; this may be due to the fact that both the reduced and oxidized form of the deposit have similar light absorbing properties (both forms being black) or, as discussed by Conway and coworkers [32] for cobalt, the major portion of the oxide film is redox inactive, reversible charge storage behaviour being confined to the outer, near-surface region of the deposit.

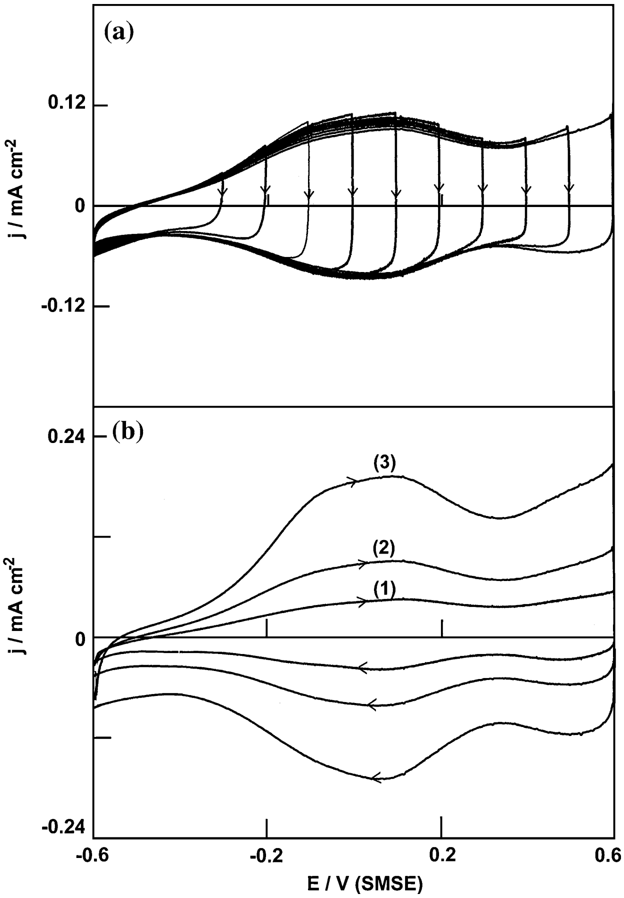

Fig. 1 Cyclic voltammograms for a hydrous Ru oxide-coated Ti electrode in 0.5 mol dm^{-3} H_2SO_4 at 25 °C: (**a**) effect of increasing the upper limit (v = 20 mV s^{-1}); (**b**) effect of increasing the sweep rate: (1) 10 mV s^{-1}; (2) 20 mV s^{-1}; (3) 50 mV s^{-1}

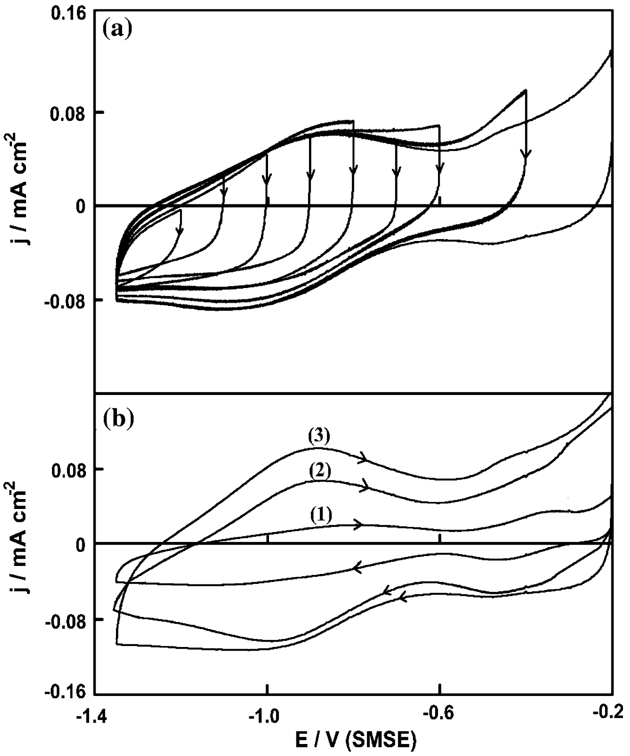

Fig. 2 Cyclic voltammograms for a hydrous Ru oxide-coated Ti electrode in 1.0 mol dm^{-3} NaOH at 25 °C: (**a**) effect of increasing the upper limit (v = 20 mV s^{-1}); (**b**) effect of increasing the sweep rate: (1) 10 mV s^{-1}; (2) 20 mV s^{-1}; (3) 50 mV s^{-1}

The maximum (E_p) of the charge storage peaks in acid (Fig. 1) and in base (Fig. 2) occurred at ca. 0.05 and −0.95 V (SMSE), respectively, i.e. on changing from acid to base, $\Delta pH \approx 12.5$ units, the peak maxima for the quasi-reversible redox transition shifted in the negative direction by ca. 1.0 V. This corresponds to a mean $\delta E/\delta pH$ shift of ca. −80 mV per unit increase in solution pH. Such behaviour, known as a super-Nernstian Ep/pH shift, is well established for noble metal hydrous oxide deposits [31] and was pointed out earlier [33] for thermally prepared RuO_2 films. When the oxidation state of the cations in the hydrous oxide is ≥ 2, excess OH^- ions are coordinated by these cations (the process may involve proton expulsion from coordinated water molecules) resulting in the framework of the porous oxide deposit acquiring a negative charge (counterions, H_3O^+ and Na^+, may be present in the aqueous regions of the layer). Raising the pH (or OH^- activity) of the solution generally increases the stability of the more oxidized (and more anionic) state and shifts the potential of the transitions involved to lower potentials. A clear-cut illustration of such behaviour is that Pt hydrous oxide films are easily reduced in acid solution but cannot be reduced completely, even at $E \leq 0.0$ V (RHE), in base [34].

The effect of cathodizing a hydrous ruthenium oxide-coated electrode at a hydrogen overpotential of ca. 0.25 V is outlined in Fig. 3 for acid and Fig. 4 for base. In both cases, the hydrogen evolution rate decreased initially to a value just below 20 mA cm^{-2}. In base, Fig. 4, this rate was maintained for 14 h; the deposit was reasonably stable, although as shown in the inset there was some loss of voltammetric charge associated with the active layer over this period. The behaviour in acid was different; as shown in Fig. 3 the rate of hydrogen gas evolution began to decay significantly after ca. 3 h and was quite low after 8 h. As illustrated in the inset in Fig. 3 the cyclic voltammogram recorded after prolonged cathodization in acid solution showed no sign of a residual Ru hydrous oxide response; the deposit was assumed to undergo gradual reduction and hence becomes detached from the surface.

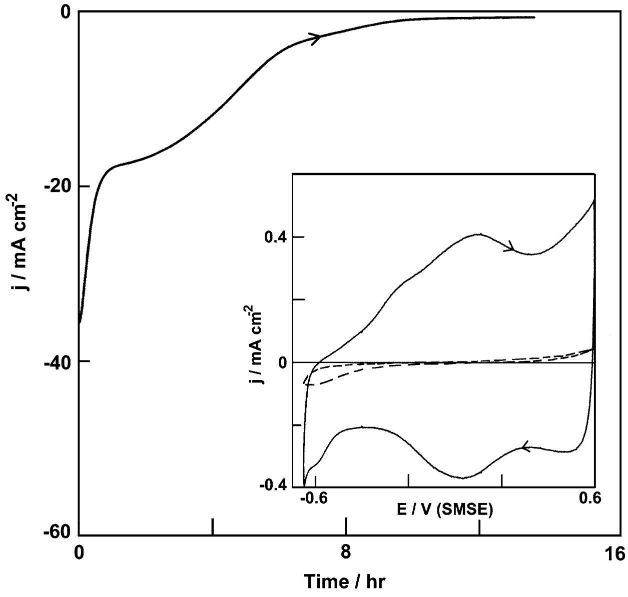

Fig. 3 Variation of the hydrogen evolution rate with time for a hydrous Ru oxide-coated Ti electrode at $E = -0.95$ V in 0.5 mol dm^{-3} H_2SO_4 at 25 °C; the inset shows cyclic voltammograms (-0.65 to 0.6 V, 20 mV s^{-1}) recorded prior to cathodization (full line) and after 14 h of cathodization (dashed line) at -0.95 V

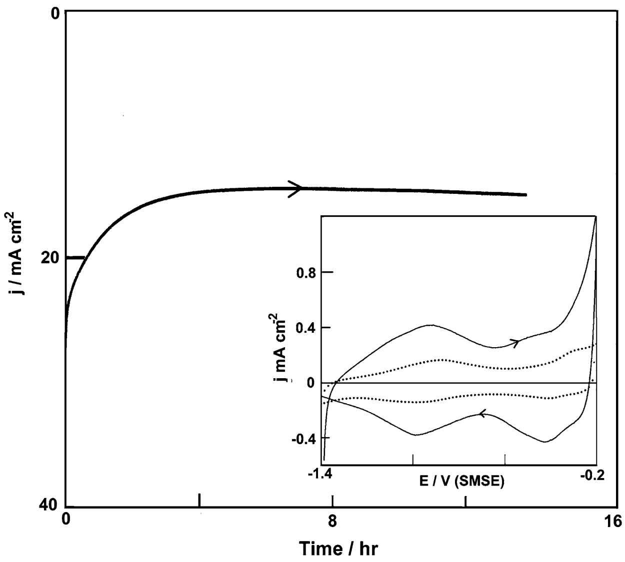

Fig. 4 Variation of the hydrogen evolution rate with time for a hydrous Ru oxide-coated Ti electrode at $E = -1.70$ V in 1.0 mol dm^{-3} NaOH at 25 °C; the inset shows cyclic voltammograms (-1.40 to -0.2 V, 20 mV s^{-1}) recorded prior to cathodization (full line) and after 14 h of cathodization (dotted line) at -1.70 V

A feature of the result in Fig. 3 is that the hydrous Ru oxide deposit maintained its hydrogen gas evolution activity for a period of ca. 4 h. The deposit was evidently reluctant to undergo reduction at -0.95 V (SMSE) despite the fact that, according to thermodynamic data [16], ruthenium has no oxide stable below 0.74 V (SHE) or ca. 0.1 V (SMSE). The inhibition of anhydrous ruthenium oxide reduction under cathodic conditions was attributed recently [20] to the intervention, as primary reduction products, of high-energy states of the metal (isolated Ru atoms or microclusters). This approach is also applicable to hydrous Ru oxide films and the converse is also assumed to apply, i.e. if a ruthenium metal deposit is in an active state it will tend to undergo oxidation in acid at E well below 0.1 V (SMSE). The oxide formed in air may be largely anhydrous, but is likely to become hydroxylated when the deposit is immersed in aqueous media. Copper deposition on Ru in an acid plating bath is then a matter of competition; ideally oxide reduction should precede copper deposition but, due to the sluggishness of the former process, this may not occur; as demonstrated here later copper deposition occurs quite readily at RuO_x cathode surfaces.

3.2 Copper deposition onto ruthenium

The basic electrochemistry of ruthenium in aqueous acid solution is quite difficult to investigate as the adsorbed hydrogen and monolayer oxide regions overlap and it is easy to produce a multilayer oxide film on the Ru surface by repeated potential cycling [35]. Examples of CV responses obtained in the present work for an electrodeposited Ru film and the Ru bar electrode in acid solution are shown in Figs. 5 and 6, respectively. In both cases the responses were relatively featureless; Ru has a strong affinity for oxygen and exposure of the surface to air is assumed to produce a thin oxide coating. Hence the responses observed in the present work (which are rather similar to some of those reported by Woods and coworkers [24]) are assumed to relate to a partially oxidized Ru surface (extensive precathodization of the electrodeposited Ru layer in the present case had little effect on the subsequent CV responses in acid solution). There are some ill-defined features evident in the present CVs, e.g. a small anodic peak at ca. −0.5 V in Fig. 5 and an increase in anodic current at ca. −0.3 V in Fig. 6 (both in the positive sweeps), but it is not clear whether these correspond to oxidation of adsorbed hydrogen, surface oxidation of exposed Ru metal or further oxidation of surface oxyruthenium species.

A typical example of a response for a thick, thermally prepared, RuO_2-coated Ti electrode in acid solution is shown in Fig. 7. According to previous accounts of this system, the main voltammetric charge is due to surface redox transitions [33], with broad peak features associated with discrete processes, e.g. a Ru(III)/Ru(IV) transition at ca. 0.0 V and a Ru(IV)/Ru(VI) transition at ca. 0.6 V in protruding oxyruthenium groups. There is a significant cathodic response in the negative sweep below −0.4 V, apparently due to either further oxide reduction, e.g. some reduction of Ru(III) to Ru(II), or reduction of some oxy-species generated in the upper region of the positive sweep (in the region above −0.2 V the anodic charge in the positive sweep exceeded the cathodic charge in the negative sweep; the opposite behaviour is evident at $E < -0.4$ V). The main point here is that this RuO_2 deposit, which is a metallic conductor, is non-reducible under cathodic conditions in aqueous solution at ambient temperature [20].

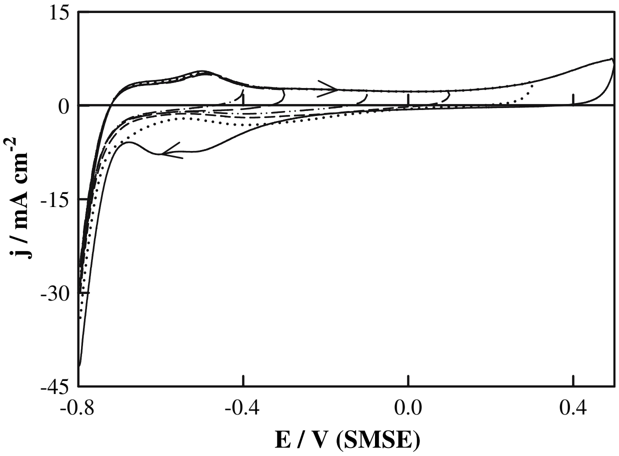

Fig. 5 Cyclic voltammetry responses, at 10 mV s^{-1}, for an electrodeposited Ru electrode in deoxygenated 1.0 mol dm^{-3} H_2SO_4 solution at room temperature: the lower limit was fixed at −0.8 V while the upper limit was raised from −0.40 to 0.50 V

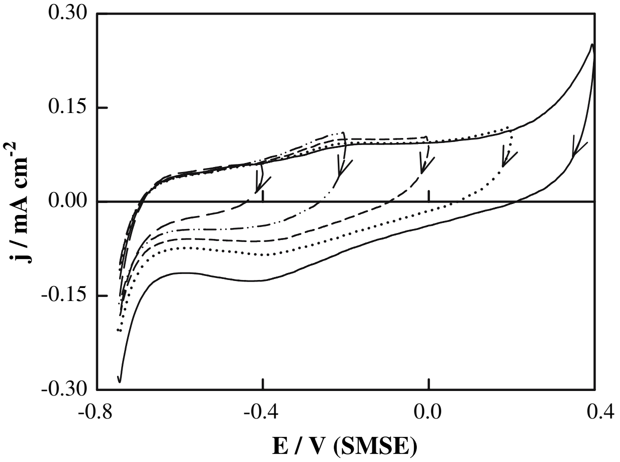

Fig. 6 Cyclic voltammetry responses, at 10 mV s^{-1}, for a Ru bar electrode in deoxygenated 1.0 mol dm^{-3} H_2SO_4 solution at room temperature: the lower limit was fixed at −0.75 V while the upper limit was raised (in 0.20 V steps) from −0.40 to 0.40 V

Some responses for an electrodeposited Ru film electrode in a copper plating solution are shown in Fig. 8. Bulk copper dissolution occurred in this case just above −0.40 V in the positive sweep. Very little copper was deposited at the lower end of the sweep, −0.41 V, unless the potential was held at the latter value. As is clear from this diagram, the charge associated with the anodic process, i.e. the magnitude of the peak between −0.4 and −0.3 V in the positive sweep, increased in proportion to the holding time at −0.41 V (or the amount of copper deposited at the latter). The dashed line response (zero holding time

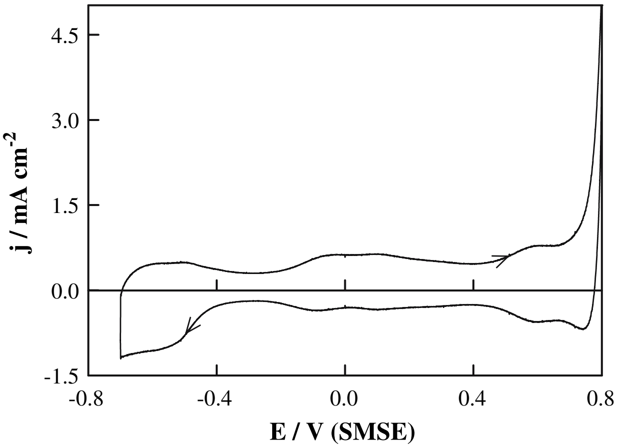

Fig. 7 Cyclic voltammograms (−0.70 to 0.80 V, 20 mV s^{-1}) for a thermally prepared RuO_2/Ti electrode in 1.0 mol dm^{-3} H_2SO_4 at room temperature

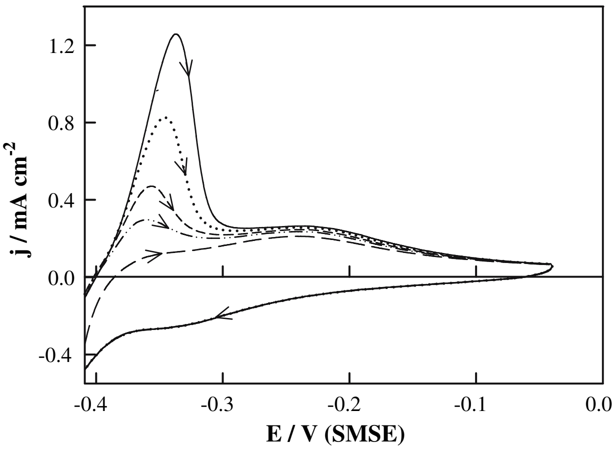

Fig. 8 Cyclic voltammograms (−0.41 to −0.04 V, 10 mV s^{-1}) for an electrodeposited Ru film in deoxygenated 1.0 mol dm^{-3} H_2SO_4 + 0.05 mol dm^{-3} $CuSO_4$ solution at room temperature; the electrode was first held at the lower limit for the following time periods (seconds): (– – –), 0; (–··–), 10; (- - - -), 20; (····), 40; (–), 60

at −0.41 V) in Fig. 8 is interesting, as it should correspond to the underpotential deposition (UPD) behaviour of Cu on Ru. For comparison with Ru, the UPD response for Cu on electrodeposited Pd is shown in Fig. 9: monolayer oxide formation on Pd in acid commences at ca. 0.15 V (SMSE) so that the UPD Cu region in Fig. 9 is virtually free of oxide interference and is relatively complex (as will be reported in detail shortly the UPD behaviour of Cu on other metals, e.g. Au and Pt, is also well defined). No such clear-cut Cu UPD responses were observed for either electrodeposited or bulk Ru surfaces (the Ru bar electrode gave similar responses to those shown in Fig. 8 for the conditions outlined in the latter).

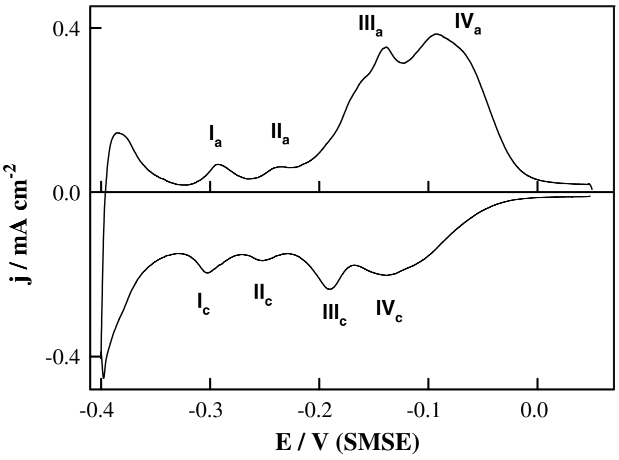

Fig. 9 Cyclic voltammetry response (−0.05 to −0.4 V, 5 mV s^{-1}) for formation and removal of UPD copper on electrodeposited Pd in deoxygenated 1.0 mol dm^{-3} H_2SO_4 + 0.01 mol dm^{-3} $CuSO_4$ solution at room temperature

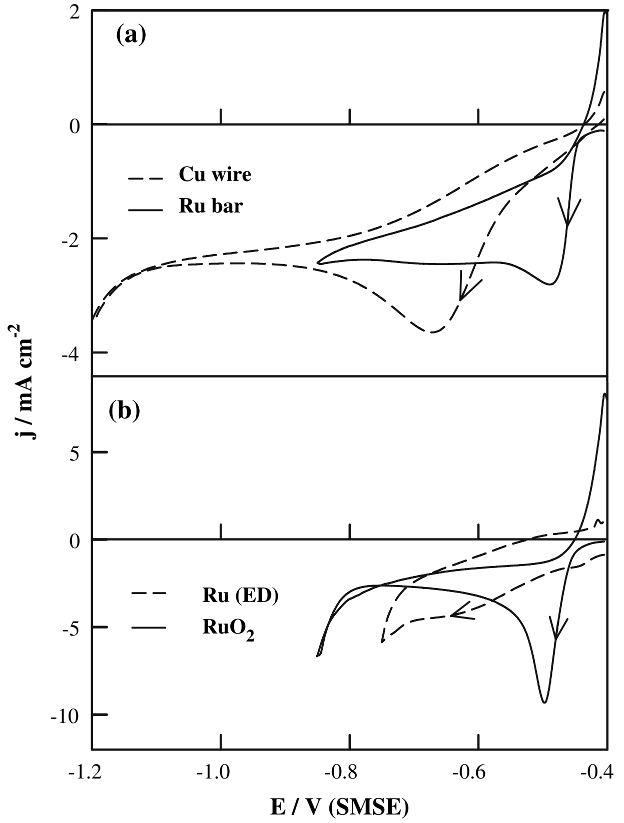

Fig. 10 First cycle (commencing at the upper limit, −0.40 V) recorded for (**a**) a Cu wire electrode (- - -) and a Ru bar (—) electrode and (**b**) an electrodeposited Ru film (- - -) and a thermally prepared RuO_2 film (—) electrode in 1.0 mol dm^{-3} H_2SO_4 + 0.05 mol dm^{-3} $CuSO_4$ solution at room temperature. The lower limit (selected to avoid vigorous H_2 evolution) was as follows: Cu, −1.20 V; Ru bar and RuO_2, −0.85 V; Ru film (ED), −0.75 V: sweep rate = 10 mV s^{-1}

Some cyclic voltammograms recorded for copper deposition at various electrodes are shown in Fig. 10. The lower limit was usually confined to −0.85 V to avoid vigorous hydrogen evolution responses (with both Ru and RuO_2); the exception was copper where the lower limit was −1.20 V and appreciable hydrogen evolution commenced only below −1.1 V. There was significant overshoot at the early stages of the negative sweep in the case of copper (dashed line in Fig. 10a). The deposition in this case commenced rather sluggishly below ca. −0.45 V but accelerated rapidly at ca. −0.6 V and the peak close to −0.7 V may be due to the disappearance of the deposition inhibition process [15] and the development of a steady-state concentration gradient at the interface. Below ca. −0.8 V, the plating rate is assumed to be transport limited but clearly there is increasing inhibition of the plating reaction in the positive sweep as the potential was increased from ca. −0.8 to −0.4 V.

The main source of inhibition of Cu^{2+} deposition on Cu above ca. −0.7 V was attributed recently [15] to the intervention, as the primary product of reduction, of a cationic species, e.g. Cu^{+}_{ads} or $Cu^{+}_{2,ads}$, at the copper surface. Further evidence to support this assumption was obtained recently from a study of the electrocatalytic properties of copper in acid [36]. Other authors have reported [37, 38] that UPD copper on gold (a metal of similar character with regard to surface properties as copper) is also cationic in character). Evidently, these cationic surface species ($Cu^{+}_{x,ads}$) create a positive field which attracts anions (as counter ions [39, 40]) but repels cations such as Cu^{2+}, and hence inhibits the plating process above ca. −0.7 V.

A remarkable feature of the responses for copper deposition on the Ru bar electrode (full line in Fig. 10a) and the thermally prepared RuO_2 deposit (full line in Fig. 10b) is that this inhibition of the plating process at the early stage of the negative sweep is apparently absent (note the sharp increase in current in both cases at ca. −0.45 V). An oxide surface is at least partially hydroxylated and therefore, as discussed here earlier, anionic in character. The latter has two effects; the negative oxide species attract Cu^{2+} ions (as counter ions, although these must compete with H_3O^+) and will tend to counteract the positive field at the interface associated with $Cu^{+}_{x,ads}$ generation. The net result is a marked reduction of the inhibition of the initial rate of copper plating at the beginning of the negative sweep.

This sharp increase in cathodic response at ca. −0.45 V in the negative sweep was virtually absent in the case of electrodeposited Ru (dashed line in Fig. 10b). Either the surface in this case was less oxidized (and hence less anionic) or there may be some immersion plating of copper accompanied by oxidation of active ruthenium (Ru*), viz.

$$2Ru^{*} + 3Cu^{2+} + 3H_2O = Ru_2O_3 + 3Cu + 6H^{+} \qquad (1)$$

(another possible reductant in this case is H_{ads}; −0.4 V (SMSE) ≈ 0.24 V (RHE) at pH = 0).

The effect of thermal pretreatment of electrodeposited Ru in air on the response recorded under plating conditions is illustrated in Fig. 11. In the initial case, where the deposit was unheated, Fig. 11a, there was a slight increase in plating rate in the negative sweep at ca. −0.45 V. After the thermal pretreatment, when the Ru surface was more extensively oxidized, Fig. 11b, the increase in cathodic current at ca. −0.45 V in the negative sweep was far more dramatic, i.e. in the initial stages copper is deposited more readily in an acid plating bath onto an oxidized, as compared with a freshly deposited, Ru surface. This effect is of a transient character as the oxide surface becomes plated with copper at lower potentials (note the low plating response over the range −0.7 to −0.5 V in the positive sweep).

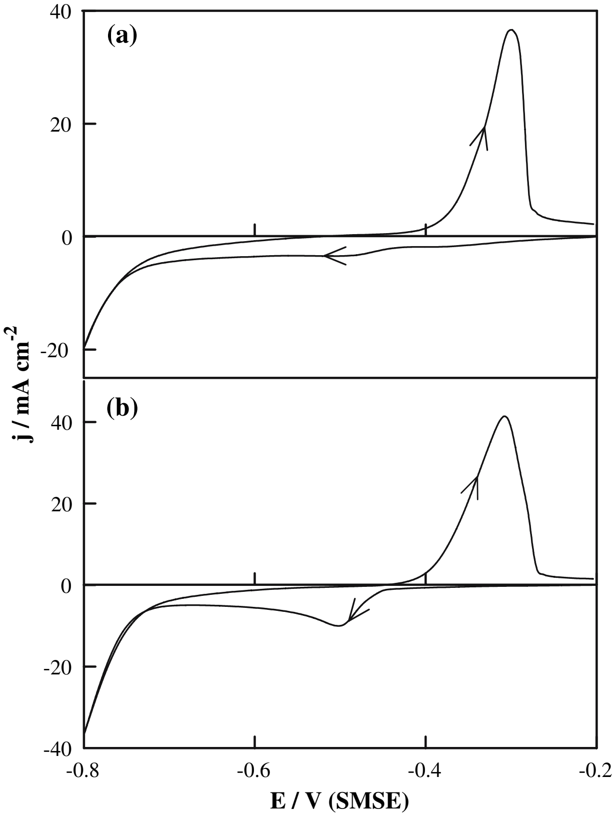

Fig. 11 Cyclic voltammograms (−0.20 to −0.80 V, 20 mV s^{-1}) for electrodeposited Ru film electrodes before (**a**) and after (**b**) mild heating in air; the electrolyte was 1.0 mol dm^{-3} H_2SO_4 + 0.05 mol dm^{-3} $CuSO_4$ solution at room temperature

4 Conclusions

Ruthenium is one of the least noble of the Platinum Group metals and its surface has a strong affinity for oxygen; this tendency to undergo spontaneous oxidation, e.g. in air, is significantly enhanced if the freshly deposited metal surface layer is in an active metastable form. Both anhydrous and hydrated ruthenium oxide deposits exhibit a marked reluctance to undergo reduction even in acid solution; this was attributed earlier [20] to the intervention of high energy states of the metal as intermediates in the reduction process. Hence it appears that unless special precautions are taken to avoid surface oxidation of the ruthenium, or to effectively remove such oxide prior to plating, copper will be deposited on an oxide film rather than on ruthenium metal. The current results indicate that at low overpotentials copper deposition commences more readily on oxidized Ru than on copper. However, the presence of oxide at the Ru/Cu interface is detrimental [9] as it results in poor trench filling and weak adhesion between the copper inlay and the ruthenium trench liner.

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