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SPECIFIC DEFECTS AND THERMOMECHANICAL PROPERTIES OF ELECTRODEPOSITED Cu FOILS

SPECYFICZNE DEFEKTY I WŁAŚCIWOŚCI TERMOMECHANICZNE ELEKTRO-OSADZONYCH WARSTW Cu

Electrodeposition of copper foils is a commercially widely used technique whose potential for producing functionally graded materials by deliberate time variation of the deposition parameters has been shown. Due to the presence of superabundant vacancies (stabilized by hydrogen) structural instabilities are strongly enhanced. More detailed knowledge of microstructural details (especially defect changes during annealing and stability at elevated temperatures) is needed for a basic understanding. Electrical residual resistivity isochrones, positron annihilation, Young's modulus and linear thermal expansion of copper foils of 35 μm thickness of different grain size electrodeposited at commercially usual rates are investigated. For all samples structural changes have been observed during the measurements, the strongest influence seems to be due to the annealing out of single vacancies (presumably by releasing hydrogen) and to grain coarsening.

Keywords: copper, thin foil, electrodeposition, microstructure, structural defects, superabundant vacancies, vacancy clusters, pores, cracks, electrical residual resistivity, positron annihilation, Young's modulus, linear thermal expansion

Elektroosadzanie warstw miedzi jest szeroko stosowaną w przemyśle techniką produkcji funkcjonalnych materiałów gradientowych poprzez kontrolę parametrów procesu wydzielania. Niestabilność struktury jest silnie uwydatniana dzięki obecności nadmiarowych wakancji stabilizowanych wodorem. Szczegółowa znajomość mikrustruktury (zwłaszcza zmian defektów podczas wygrzewania oraz stabilność w podwyższonych temperaturach) jest konieczna dla zrozumienia procesu.

Przedmiotem badań była izochronowa szczątkowa oporność elektryczna, anihilacja pozytonów, moduły Younga oraz liniowa rozszerzalność termiczna eketroosadzanych (przy

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szybkościach osadzania stosowanych w przemyśle) warstw Cu o grubości 35 μm i o zróżnicowanej wielkości ziarna. Zmiany strukturalne wszystkich próbek obserwowano podczas pomiarów, przy czym najsilniejszy wpływ spowodowany wygrzewaniem wydaje się być związany z pojedynczymi wakacjami (przypuszczalnie przez uwalnianie wodoru) i rozrostem ziaren.

1. Introduction

Electrodeposition is one of the most important technology to tailor materials for desired properties and various geometries [1, 2]. Metal deposition on substrates by high current densities is widely in use for the industrial supply of thin foils for micro-electro-mechanical systems (MEMS), usually heterostructures e.g. in the electronic and automotive industry [3, 4]. The complex process is of interdiciplinary nature [5], the particular composition and microstructure of the deposit is governed by various parameters, among them the composition of the electrolyte (including additives), the overvoltage and the temperature. In particular, characteristic combinations of composition, particle size, defect concentration (e.g. vacancies, voids, impurities, dislocations, twin boundaries, cell and grain boundaries) and texture can be achieved. Thus, a systematic time variation of the deposition parameters is suitable to obtain functionally graded materials as reported in a few cases [e.g. 6]. The deliberate applicability is restricted mainly by two facts. Firstly, the inevitable co-deposition of hydrogen together with the metal is likely to have a severe impact on the defect structure and stability, especially on the vacancy type defects which are not easily investigated. Further on, all the influence on particle size, defects and texture are coupled. Thus the possibilties to taylor materials are severely restricted.

Thus, a prerequisite for the use of electrodeposition for producing functionally graded materials is the improvement of the principle understanding of the obtained structures, especially vacancy type defects of concentration up to 1% [7] at room temperature, hydrogen influence (by co-deposition), influences of additives and high concentration of grain boundaries.

In this context, the recently published works on superabundant vacancy-hydrogen complexes [8, 9] are helpful. The equilibrium concentration of vacancies bound to hydrogen atoms is considerably higher than that of unbound vacancies (as also deduced by positron annihilation in Nb [10], Ni and Fe [11]). For electrolytic powders and electrodeposited (ED) Cu, a disintegration shows two peaks, the lower one at 330oC and the upper one at 500°C [9]. Below, the highly enhanced vacancy concentration seems to cause a permanent instability of metastable structures in ED Cu even at room temperature.

This paper aims to contribute to the understanding of the effect of these deposition-characteristic defects by the measurements of electrical residual resistivity, positron lifetime, Young's modulus, ultimate tensile strength, elongation to fracture and thermal expansion after different thermal treatment.

2. Experimental

Freestanding 35 μm thick Cu foils industrially produced using electrodeposition parameters in order to obtain small grain sizes, stripped off from the chromium substrate and annealed for 30 min at 180°C have been supplied by Gould Electronics. The resulting grain sizes were 0,3 μm (CHAN), 0,7 μm (DF) and 2 μm (HTE 342T), the in-plane texture was random. Defect structures have been given elsewhere [12]. For comparison, a rolled foil with 4,5 μm grain size (with $<100>$ plus $<111>$ texture in-plane) and a standard reference material for thermal expansion have been used.

Electrical resistivity isochrones were obtained (for room temperature and 4,2 K as measurement temperatures) with a four probe DC method to monitor defect changes.

Positron lifetime measurements have been done depth sensitively (at the deposite surface stripped off the Ni substrate) by the pulsed low-energy positron beam system (PLEPS) at the Bundeswehrhochschule Neubiberg [13] for the characterization of open volume defects by positron lifetimes.

Elastic and plastic properties were measured in a microtensile machine with specialized gripping and mounting equipment described elsewhere [14] on 10 mm broad strips. The linear expansion was determined [14] for samples in thermal contact (by vacuum oil) with the temperature controlled plate of a furnace. A joint investigation of Young's modulus E and linear thermal expansion coefficient α can shed light on the presence of larger voids and holes. Both values are known to be coupled in metallic samples by the Grüneisen relation, which can be assumed to be valid for a moderate concentration of small structural defects (on an atomic scale) as vacancies. This relation will break down for large voids or holes as Young's modulus is considerably reduced, whereas linear expansion will be less affected.

All strain measurements have been carried out contactlessly by a laser speckle correlation method described elsewhere [14] using a base length of 20 mm.

3. Results and discussion

Fig.1 shows the results of electrical resistivity isochrones of ED Cu annealed previously for 30 min at 180°C. Annealing steps were 25°C, the holding times 10 min. The CHAN and DF curves (initial grain size 0,3 μm and 0,7 μm, respectively) show a monotonous decrease as usually expected by the defect annealing and grain coarsening. The HTE 342T curve (initial grain size 2 μm) reaches a shallow minimum and rises again. As the grains are the largest, in this case, the resistivity drop caused by the grain growth is the smallest. Thus the overall resistivity is dominated by a rise very likely due to a rearrangement of defects (either impurity defects from additives or more likely to the disintegration of hydrogen from the vacancies, which is known to occur in this temperature region [9]).

A first positron investigation performed on this particular sample should reveal the positron-trapping defects. From the positron data obtained by PLEPS with a resolution

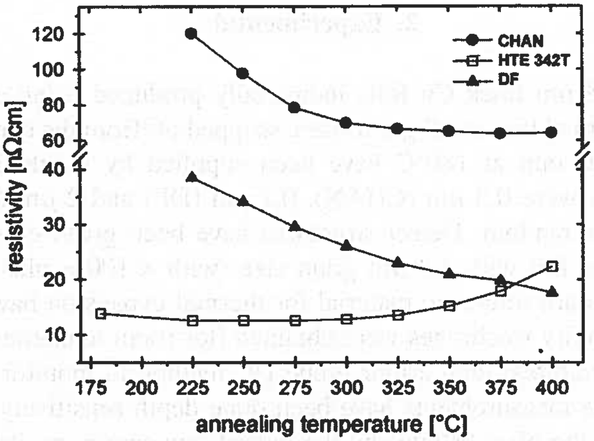

Fig. 1. Resistivity isochrones for electrodeposited Cu foils for holding times of 10 minutes. Between the subsequent anneals resistivity measurements were performed at 4.2 K. For sample description see text

function of typically 230 ps, usually up to three lifetime lines can be determined in an unconstrained lifetime fit. In our investigation a consistent fit was obtained for the copper sample annealed at 180°C for the case of four lifetimes (accepting increased error margins). Similar fits were possible after annealing at 275°C and 325°C (slightly above the resistivity minimum). The data characteristic for a depth of 0,2 to 0,3 μm below the deposition surface are shown in Tab.1.

TABLE

Intensities and lifetimes each averaged from 4 fits. The lifetimes averaged over all three samples are $\tau_2^{av} = 170 \pm 6$ps, $\tau_3^{av} = 360 \pm 20$ps

Annealing temperature	180°	275°	325°
I_1 [%] (τ_1)	21 ± 1 (52 ps)	22 ± 1 (49 ps)	40 ± 3 (70 ps) Cu lattice
I_2 [%] (τ_2)	60 ± 6 (175 ps)	51 ± 9 (157 ps)	47 ± 4 (196 ps) Vacancy
I_3 [%] (τ_3)	19 ± 5 (380 ps)	23 ± 5 (318 ps)	21 ± 3 (394 ps) Vacancy cluster

For a further discussion, the possible interactions of hydrogen with vacancy type defects are important. Whereas in Cu samples prepared from the melt, excess vacancies (from quenching or plastic deformation) tend to coagulate into planar vacancy loops [15] or to anneal out at sinks, in contrast to ED material, it is known that at room temperature concentrations of vacancies as high as 1% may survive [7]. A new explanation has emerged by introducing superabundant vacancies (see also [10, 11]) in thermal equilibrium of similar room temperature concentrations [9] in electrodeposits, based on the mechanism of a strong reduction of the formation enthalpy of vacancy-hydrogen complexes. Thus a mutual stabilization of vacancies, vacancy clusters and hydrogen content occurs in Ni and Cu.

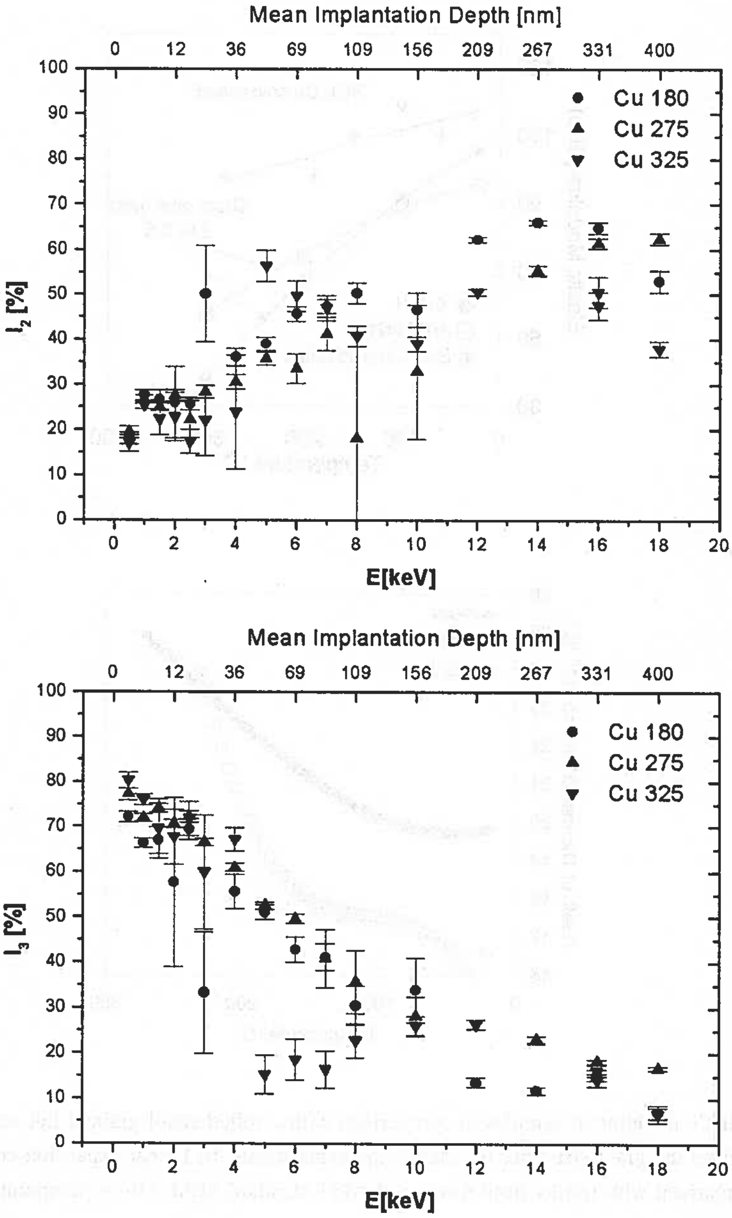

Fig. 2. Intensity of lifetime lines characteristic for vacancies (a) and vacancy clusters (b) in electrodeposited Cu foils as function of positron implantation depth. The inset gives the annealing temperature in °C

The following picture seems consistent with these ideas, as well as with the positron lifetimes and intensities and their variation with implantation depth shown for the defect intensities in Fig.2ab. It seems that there exist hydrogen stabilized vacancies at high

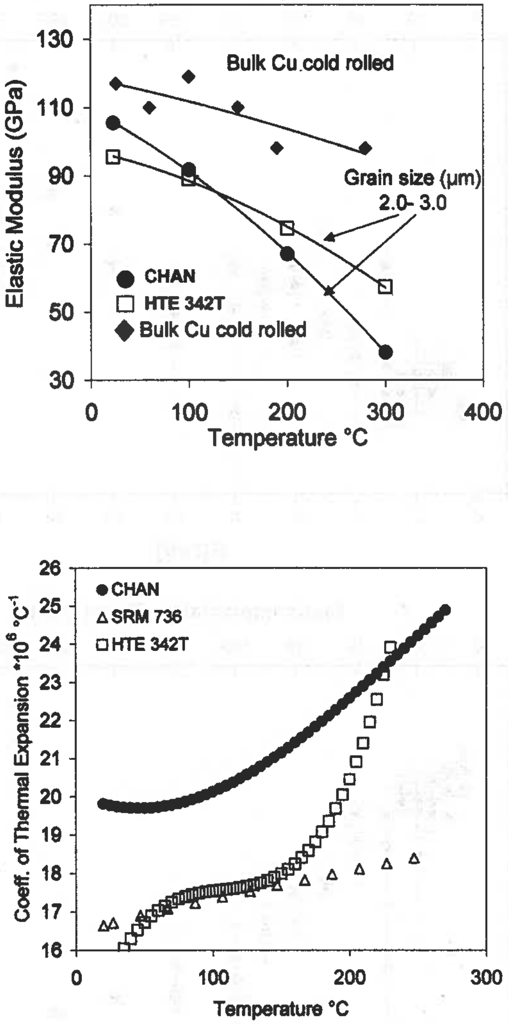

Fig. 3. a) Young's modulus of samples in comparison with a rolled small grained foil vs. temperature. The inset gives the grain size after the end of the experiments, b) Linear expansion coefficient in comparison with results from 6 mm rod NIST standard SRM 736 vs. temperature

(equilibrium) concentrations trapping more than half of the positrons (Fig.2a). These defects are depleted at the surface. Microvoids (vacancy clusters) at triple points of the grain structure are also present throughout the sample with higher concentration near the surface (Fig.2b) where the grain size is reduced [7]. Pores seem to be stable only next to the surface. The influence of hydrogen bound to vacancy-type defects is a reduction of positron lifetime [10, 11]. Thus the pore diameter seems to exceed 0,7 nm which would correspond to the lifetime for hydrogen-free pores [16]. The lifetime

τ_1 of positrons annihilating in the Cu lattice is considerably reduced compared with defect-free material indicating the validity of the fit according to the standard positron trapping model [17]. With annealing up to 325°C, the vacancy concentration is reduced (presumably due to hydrogen release) and the vacancies anneal out mainly as vacancy clusters but due to the recrystallization, the over-all cluster concentration does not change significantly.

For higher annealing temperatures, the number of defect lines seems to grow but they are not separable any more. Thus, the positron data yield no direct evidence for the process which increases the electrical resistance.

The data for Young's modulus and linear expansion are shown in Fig. 3a and Fig.3b, respectively. The unusual drop of E accompanied by an even more dramatic rise in α (sample HTE 342T) can be understood based on the inevitable microstructural changes during the measurements influencing the vacancy clusters in the weak grain boundary region. The grain sizes after the measurements were between 2 and 3 μm for both CHAN and HTE 342T samples indicating a large difference in stability. Especially the occurrence of cracks at the clusters [18] could explain the data obtained, while crack closing could be inhibited by hydrogen. The failure of Grüneisen relation is a consequence [19]. Also the observed fracture surface is in accordance with the idea of cracks occuring in the grain boundary area.

4. Conclusions

- In commercial Cu electrodeposits of 2 μm grain size annealed up to 325°C vacancies and small vacancy clusters (very likely at triple intersections of grains) are the main defects trapping positrons. Only near the surface additional voids are detected fom positronium lifetimes.
- Compared with rolled and quenched samples (where vacancies anneal out into planar loops) vacancies are stabilized by hydrogen and agglomerate to three- dimensional clusters. At temperatures where hydrogen is released the electrical resistivity of vacancies seems to rise.
- A strong drop of Young's modulus after annealing at 300°C accompanied with an even stronger increase of linear thermal expansion can be explained by the occurrence of cracks due to stress concentrations at clusters. Crack closure could be inhibited by a hydrogen influence, too.
- Lifetime calculations for hydrogen-vacancy complexes in Cu, high-precisison lattice constant determinations and investigations of samples annealed above 500°C should be performed for a support of these results and a further clarification.

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