

Electrochemical Deposition of Copper Phosphides

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Summary. Methods for preparation of copper phosphides at ambient temperatures by electrodeposition are presented. From $P_4/PCl_3/Acetonitril/TBA-BF_4/Cu^+$ (solvated) Cu_3P and Cu_3P_2 can be obtained at different deposition potentials.

Keywords. Copper phosphides; Electrodeposition.

Elektrochemische Abscheidung von Kupferphosphiden

Zusammenfassung. Es werden Verfahren zur Herstellung von Kupferphosphiden bei ambienten Temperaturen beschrieben. Aus der Anordnung $P_4/PCl_3/Acetonitril/TBA-BF_4/Cu^+$ (solvasiert) können Cu_3P und Cu_3P_2 bei verschiedenen Abscheidungspotentialen erhalten werden.

Introduction

We were interested in the preparation of compact films of copper phosphide(s), either semiconducting and adherent to suitable support materials (in the course of a study of solar cell materials) or metallic (in connection with the preparation of amorphous alloys [1, 2], or the production of phosphor bronze) [3]. Copper phosphides of different stoichiometries can be obtained by various routes [4], e. g. by reacting the elements at elevated temperatures [5], by reaction of CuS with PH_3 [6], of $[CuCl_2 \cdot PH_3]^-$ with NH_3/H_2O [7], of Cu with PCl_3 [8, 9] or of $Cu(NO_3)_2$ with P_4 in organic phase [10]. Electrolysis of phosphate-containing melts at high temperatures is a general way of synthesis of metal phosphides [11, 12]. Chêne obtained Cu_3P and Cu_2P by this way [13]. Copper phosphides do not seem to have been ever obtained at low temperatures. Therefore, we checked the possibilities of electrodeposition at ambient temperature.

Experimental

All chemicals used were of AR grade, the solvents and supporting electrolytes dried by conventional means. Cyclovoltammograms were run using a Wenking Laboratory Potentiostat Model LB 75 L, a Wenking Model VSG 72 Scan Generator and a Hewlett Packard 7004 B x, y-Recorder.

Preparative electrodepositions were done in undivided, thermostatted cells with copper or titanium sheet metal working electrodes, platinum counter electrodes, and saturated calomel reference electrodes

from stirred electrolytes. EDX data and microphotographs were obtained with a JEOL SCM 35 C connected with energy dispersive X-ray analyser (EDX, EG & Ortec system 5000). X-Ray powder diffraction data were obtained on a Guinier Diffractometer Huber 642. Elemental analyses were done in the Microanalytical Laboratory of our institute.

Results and Discussion

Comparable to the electrodeposition of metal chalcogenides starting from metals or metal ions and H_2E , HE^- , E^{2-} or E_2^{2-} [$E=S, Se, Te$] in aqueous electrolytes [14] first we studied the oxidative formation of copper phosphides from copper substrate and PH_3 containing solutions. Since PH_3 is significantly soluble in acetic acid at room temperature we started with this acid, $1 \cdot 10^{-2} M Bu_4NBF_4$ and saturated with PH_3 and a copper anode. Table 1 lists the relevant experimental data and the atomic composition as determined by EDX.

The films grown out of the substrate were not homogeneous with strongly varying and high Cu/P ratios of 10.5 ± 5.2 . As with electrodeposited amorphous $Ni_{76}P_{24}$ voids are observed, which may be filled with PH_3 , and which may act as sites for fracture nucleation [15]. PH_3 is relatively inert and in order to activate it and to impart electrophilic properties we used Cu(I) halides, which are known to

Table 1. EDX data for deposits obtained at different experimental conditions on Cu anodes

Film No.	i [mA/cm ²]	E [V](SCE)	T [°C]	Atomic composition	
				Cu (%)	P (%)
1	3.0	1.2	25	84	16
2	3.0	1.2	50	80	20
3	2.5	0.9	70	94	6
4	2.0	0.8	80	88	12
5	2.0	0.8	30	92	8
6	1.5	0.4	50	87	13

Table 2. EDX data of copper/phosphorus layers electrodeposited from $CuCl/PH_3$ /ethanol on Cu anodes at room temperature

Film No.	i [mA/cm ²]	E [V](SCE)	Atomic composition	
			Cu (%)	P (%)
7	5.4	-20	68	8
8	2.5	-10	81	14
9	5.0	-6	80	12
10	2.5	-5	88	10
11	7.0	-4	84	12
12	2.0	-4	no deposition	
13	2.0	-3	no deposition	

form weak complexes in alcoholic solution [16] and which can be hydrolyzed to yield copper phosphides [17]. Therefore, next we studied the electrodeposition of copper phosphides from $\text{CuCl}/\text{PH}_3/\text{ethanol}$ solutions under varied conditions, listed in Table 2.

Again high Cu/P ratios of about 7.3 ± 1.5 , however, much less varying in composition were obtained. Future studies shall bring more information.

In order to avoid the possibility of inclusion of H_2 or PH_3 in voids of the copper phosphide films, we investigated the cathodic deposition of copper phosphides from aprotic electrolytes. A variant of electrochemical metal chalcogenide syntheses starts with the elemental chalcogens S, Se, and Te dissolved or suspended in organic solvents [14], however inclusions of "hetero atoms" originating from organic solvents have to be expected in the films. Therefore it seemed appropriate to choose an aprotic, relatively inert solvent and electrolyte system with as few "hetero atoms" as possible.

It is known that PCl_3 dissolves P_4 at room temperature. At high temperatures it even reacts with metallic copper to yield copper phosphides and CuCl [6]. PCl_3 is nonconducting, but can be reduced polarographically in $\text{Me}_4\text{NCl}/\text{CH}_3\text{CN}$ at $E_{1/2} = 0.93 \text{ V}$ (vs. Hg pool) [18]. In its cyclovoltammogram we observed a reduction peak at -0.98 V (SCE) at Pt in $1 \text{ M Bu}_4\text{NBr}/\text{CH}_2\text{Cl}_2$. Reduction of PCl_3 in preparative scale in $0.3 \text{ M Bu}_4\text{NCl}/\text{HMPT}$ at Pt electrodes at -1.1 V (Ag/AgCl) yielded red-brown deposits with P contents between 46.3 and 74.2% and chlorine as predominant residue [19], so that formation of P_2Cl_4 or some other lower chloride together with elemental phosphorus can be assumed. Polarographic reduction of

Table 3. EDX data for copper phosphides electrodeposited on Cu cathodes at room temperature

Film No.	i [mA/cm ²]	E [V] (SCE)	Atomic composition	
			Cu (%)	P (%)
14	12	-1.3	67	30
15	6	-1.0	67	32
16	5	-0.8	76	24
17	1	-0.8	72	24
18	3	-0.7	76	22

Table 4. EDX data for copper phosphides electrodeposited on Ti cathodes at room temperature

Film No.	i [mA/cm ²]	E [V] (SCE)	Atomic composition	
			Cu (%)	P (%)
19	3.5	-0.8	74.5	24.5
20	2.0	-0.8	75	25
21	5.0	-0.75	60	40
22	2.0	-0.75	56	44

P_4 in $[Bu_4N]ClO_4/CH_3CN$ occurs at $E_{1/2} = -1.73$ V (vs. Hg pool) [20]. On the other hand P_4 dissolved in PCl_3 is nonconducting [21]. The cyclic voltammogram of a solution: 1 mM P_4 , 10 mM PCl_3 , 0.1 M $[(n\text{-Butyl})_4N]BF_4$ in CH_3CN ($v=100$ mV/s) shows a reduction peak at -0.85 V (SCE) at a Pt cathode and in the subsequent backward scan an oxidation peak at ca. -0.35 V. Since this peak arises only in the back reaction it can be assigned to the oxidation of a reaction product of some electrogenerated species with P_4 or PCl_3 . The action of reducing agents on PI_3 and PBr_3 produces P_2X_4 , therefore our electrolyte solutions possibly contain P_2Cl_4 , which for example is described as significantly more reactive towards Hg^0 than PCl_3 [22], and which is plausible to assume as reactive species in our solutions.

After repeatedly varying the experimental conditions for electrodeposition – the use of PBr_3 for example did not bring improvements – we obtained well adherent layers of metallic lustrous Cu_3P_2 or black Cu_3P on copper or titanium

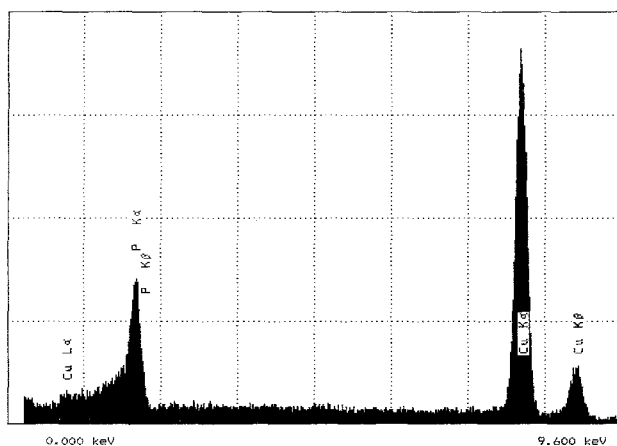


Fig. 1. EDX energy/intensity spectrum of film no.20 of Table 4

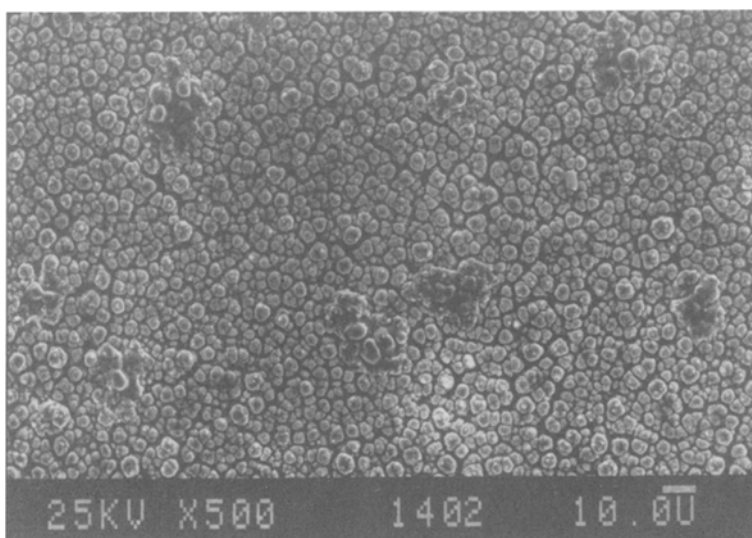


Fig. 2. SEM picture of film no.20 of Table 4 (length of bar = 10 μ m)

cathodes using a copper injection anode and the electrolyte system $P_4/PCl_3/AN/TBA-BF_4/Cu^+$ (solv.). Omitting the P_4 , i. e. using only $PCl_3/AN/TBA-BF_4$ with a copper injection anode or with added copper salts no phosphorus could be detected in the deposits by EDX analysis. Table 3 shows the microprobe data of the as-deposited films (on Cu cathodes) obtained at different current densities and potentials. At -0.8 V (SCE) we obtained black, adherent layers of Cu_3P (film no. 15, 17, 18) on Cu cathodes having a thickness of ca. $1 \mu m$. However, the EDX analyses were not conclusive, because the copper support might influence the results. Therefore, we turned to titanium supports.

Before use the Ti plates were mechanically polished with fine emery paper, treated with $0.5 M$ NaOH for 5 min, washed with de-ionized water, and finally cleaned ultrasonically in acetone.

Again we obtained Cu_3P under similar experimental conditions (Table 4).

The EDX spectrum of the nearly stoichiometric Cu_3P (film no. 20 of Table 4) is shown in Fig. 1. These films were well adherent, black and visually uniform. Fig. 2, a SEM picture of the surface, shows a finely granular surface. At slightly lower potential the stoichiometry Cu_3P_2 is attained. The electrodes have the silvery luster of that "metallic" copper phosphide.

Characterization of crystallinity and structure was carried out by X-ray powder diffractometry. For these measurements the films were scratched off the Ti or Cu

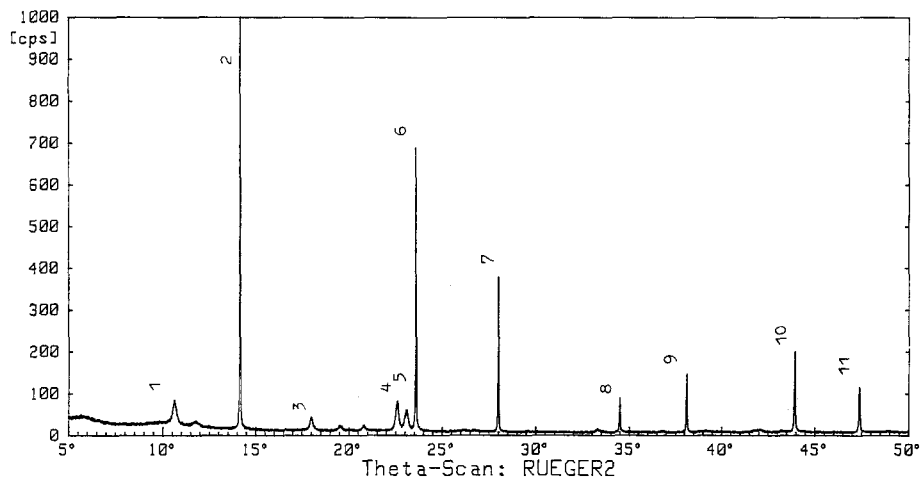


Fig. 3. X-ray diffraction patterns of the Cu_3P film as deposited, film no.20 of Table 4. Peaks 1, 2, 6–11 originate from the Si standard

Table 5. Comparison of calculated and standard d values (film no. 20 of Table 4 for Cu_3P)

Peak No.	Theta (deg)	Max. (cps)	d (calc.) (Å)	d (standard) (Å)
3	18.041	21	2.487	2.480
4	22.602	61	2.004	2.001
5	23.059	39	1.996	1.950

substrates and fixed to a polyethylene foil with Si as standard substance. The diffraction angles (2Θ) corresponding to the X-ray peak intensities were identified and the calculated values compared with standard d values from JCPDS cards [23] (Fig. 3 and Table 5).

Table 5 shows the three main Cu_3P peaks exactly corresponding to the calculated d values of the sample "film no. 20 of Table 4". X-ray investigations of a sample deposited on copper sheet showed the greater part of the Cu_3P to be amorphous, this resulting in low intensities. Thermal treatment of this film only slightly improved the crystallinity by annealing. We do not find evidence for the deposition of a simple mixture of elemental Cu and P. For elemental analyses selected layers were scratched off the substrate and dissolved. Complete dissolution occurred only on boiling in conc. nitric acid for 1 h. This behaviour is consistent with literature data of Cu_3P . The small sample sizes prevented exact analyses, however, essentially the same results were found as with EDX analyses. A chlorine content of 2–4% in the films sometimes observed can be lowered to $\ll 1\%$ by thermal treatment.

Conclusion

We present a novel, ambient temperature deposition process for copper phosphides, which is applicable to other phosphides, too. Although the reaction mechanism is not yet fully understood, some facts can be summed up:

a) The source of copper ions does not seem to be crucial, b) use of $\text{PCl}_3/\text{AN}/\text{TBA-BF}_4$ does not lead to phosphide layers, only with $\text{P}_4/\text{PCl}_3/\text{AN}/\text{TBA-BF}_4$ and copper ions dissolved therein phosphide film are obtained, c) P_2Cl_4 as reactive intermediate seems plausible, d) the layers are not mere mixed deposits of elemental Cu and P, e) by careful choice of the deposition potential the formation of Cu_3P_2 or Cu_3P can be preferentially achieved (s. Table 4).

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