

# CHEMICAL ETCHING OF $\text{CuInSe}_2$ ABSORBER SURFACE FOR MONOGRAN LAYER SOLAR CELL APPLICATION

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**ABSTRACT:**  $\text{CuInSe}_2$  monograin powders with different molecularity ( $\text{Cu/In} < 1$  and  $\text{Cu/In} > 1$ ) were subjected to various chemical treatments with several etchants (HCl, KCN, KOH in ethanol and  $\text{NH}_3$ ) to modify crystal surface and determine the effect of those modifications on CdS/ $\text{CuInSe}_2$  heterojunction quality. We found differences in the influence of etchants on  $\text{CuInSe}_2$  materials with different molecularities (Cu-rich and In-rich). The  $\text{NH}_3$  treatment of Cu-rich  $\text{CuInSe}_2$  absorber material depleted its surface from copper and selenium and led to the decreased values of open-circuit voltage. KCN dissolved preferentially copper as from In-rich as copper-rich absorber surfaces and, as a result, solar cell fill factors improved. HCl etching removed preferably indium. The cells on the base of HCl treated absorber material showed higher values of currents, but the values of open circuit voltages were lower than the cells on the base of KCN treated absorber material. KOH-in ethanol etching removed preferentially Se and solar cell  $V_{oc}$  had decreased values. The possible changes in surface defect structure are discussed.

**Keywords:**  $\text{CuInSe}_2$ , Monograin powder, Etching

## 1 INTRODUCTION

Ternary semiconductor compound  $\text{CuInSe}_2$  (CIS) is one of the most promising absorber materials for solar cells. The active interface of  $p\text{-CuInSe}_2/n\text{-CdS}$  plays the key role in their performance. Therefore, the quality of CIS surface cleaning and/or chemical etching before CdS deposition is very important. The effect of chemical treatment depends on concentration, temperature and the chemical nature of the etchant, sometimes also on the oxygen content in the solution [1]. The chemical nature of the etchant has a dramatic influence on both, surface composition and interface chemistry [2]. In this paper we present the results of our studies on the chemical surface etching of  $\text{CuInSe}_2$  monograin powders. The choice of chemical reagents used in this study based on the following considerations: 1) KCN solutions are well-known and everywhere used as selective etchants for copper binary phases and for elemental S and Se [3,4]; 2) HCl and  $\text{NH}_3$  treatments are used as processes for removal of surface oxides [1,5] and In-rich OVC layer [6]; 3) Etching in KOH-in-ethanol solution is essential in the monograin layer technology for releasing the crystal surfaces from organic binder (polyurethane) [7]. The powders etched in different etchants were later used as absorber material in monograin layer solar cells and the influence of chemical etching on their output characteristics was studied.

## 2 EXPERIMENTAL

$\text{CuInSe}_2$  powder materials were synthesized from Cu-In alloy and Se in the liquid phase of molten fluxes. More details about this process can be found elsewhere [8]. In order to restore the grain surface and modify the defect structure, the as-grown powders were post-treated in selenium and/or sulfur vapor in two-zone quartz ampoules where the vapor pressure in the whole system is determined by the temperature of Se (S) source at the lower temperature end of the ampoule. The sulfurization of  $\text{CuInSe}_2$  powder crystals leads to the formation of a higher bandgap surface region that is the presumption for devices with the higher values of open circuit voltages ( $V_{oc}$ ) [9]. After selenization and/or sulfurization, the

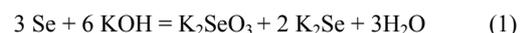
powders were divided into several parts and each of them passed through different etching. As etchants we used the aqueous solutions of concentrated HCl, 10% aqueous KCN, 5% KOH in ethanol (KOH-EtOH), and 2M  $\text{NH}_3$ . All the etchings were preceded at room temperature. The composition of leaching solutions was analyzed polarographically and the bulk composition of powders was determined by energy dispersive spectroscopy (EDS). Surface composition was studied using X-ray photoelectron spectroscopy (XPS). The monolayer of chemically treated powder crystals was embedded into polyurethane (PU), which has to be removed from the crystallite surfaces in the contact areas. CdS was deposited onto the released surface of crystallites from chemical bath. For cell completion, thin  $i\text{-ZnO}$  and conductive ZnO: Al were deposited by r. f. -sputtering. The photovoltaic properties of graphite/ $\text{CuInSe}_2/\text{CdS}/\text{ZnO}$  solar cell structures were characterized using the I-V measurements under  $100\text{mW}/\text{cm}^2$  illumination.

For the photoluminescence (PL) measurements the closed-cycle He cryostat ( $T = 10 - 300\text{ K}$ ) and the He-Cd laser were used. The PL signal was detected using a standard lock-in technique, the computer-controlled SPM-2 grating monochromator ( $f = 40\text{ cm}$ ) and an InGaAs detector. The signal detected was corrected in conformity with the grating efficiency and detector sensitivity spectra.

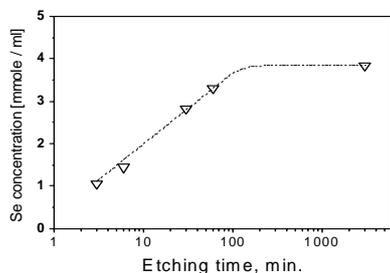
## 3 RESULTS AND DISCUSSION

### 3.1 Etching of Cu-rich powder

In the monograin layer solar cells the absorber crystals are embedded into polyurethane (PU). The contacting areas of crystals are released from PU by etching with KOH-EtOH. Polarographic analysis showed that the etching solutions of copper-rich (Cu:In:Se = 25,6 at.%, 24,2 at.%, 50,2 at.%) powders contained only selenium (see Fig. 1). The removal process of the excess selenium from the material can be described by the reaction:



As a result, the crystal surfaces should remain metal-rich. All solar cells made from KOH- etched powders had the lowered values of open-circuit voltages and short circuit currents in comparison with those made from non-etched materials. Already 5 sec. etching of the material with

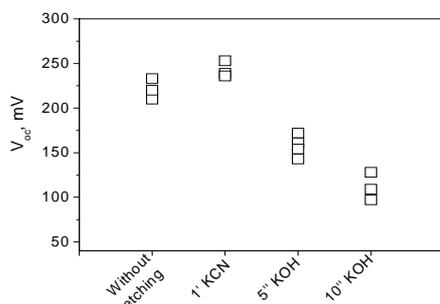


**Figure 1:** Correlation between the Se concentration in KOH-EtOH etching solution and etching time.

KOH-EtOH decreased the value of  $V_{oc}$  more than 50 mV (see Fig. 2). Consequently, the removal of PU by KOH-EtOH etching is extremely critical for further success in monograin layer technology.

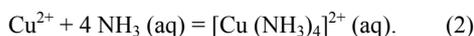
In order to eliminate the semimetallic copper selenide phases and to improve the semiconductor behaviour of Cu-rich CIS material, chemical treatments in KCN solution have been performed.

The KCN etching of Cu-rich monograin powders resulted in improved solar cell performance (see Fig. 2).



**Figure 2:**  $V_{oc}$  of monograin layer CIS solar cells made from Cu-rich powders after etching in different etchants.

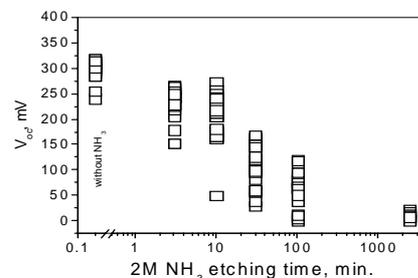
$NH_3$  solution is known as an effective solvent for the removal of surface oxides and the preferential etching of indium [2, 10]. The authors of [7] showed that  $NH_3$  dissolves preferentially the In-rich, so called ordered vacancy compound ( $CuIn_3Se_5$ ) layer from the surface. On the base of XPS results they found that In-excess layer disappeared after 1-hour treatment in 1 M  $NH_3$  aqueous solution at 60°C, leaving behind the surface with nearly 1:1:2 composition. In our experiments we found in the leaching solutions of copper-rich monograin materials copper and selenium (Cu/Se concentration ratio was between 1.4-2.4) and low content of indium. The dissolution of copper from the material in aqueous ammonia solution could be described by the formation of soluble copper-ammonia complex ions ( $[Cu(NH_4)_3]^{2+}$  and  $[Cu(NH_4)_2]^+$ ):



Kessler et. al. [1] proposed that indium dissolution

proceeds through the formation of oxides which are soluble in ammonia solution. Prerequisite for this is the dissolved oxygen in the solution. Indium oxide is known as native oxide on CIS surface. Therefore the oxidation - dissolution process should proceed on In-rich  $CuInSe_2$  surface layers much faster than on Cu-rich layers. In monograin powders every grain is formed in growth process as an individual micromonocrystal in isothermal equilibrium condition by the liquid phase transport of the material. Thereby the homogeneity of the composition of CIS crystals in the whole powder is high. This might be the reason for different results of in our studies and the ones presented in [1], where also slightly Cu-rich samples were used but large amount of indium loss was detected.

From the results of the present study it can be concluded that the  $NH_3$  treatment of Cu-rich  $CuInSe_2$  absorber material depletes surface from copper and selenium. As a result the open-circuit voltage of solar cells decreased continuously with the variation of  $NH_3$  etching time from 3 to 100 minutes (see Fig. 3).



**Figure 3:** Open circuit voltage ( $V_{oc}$ ) as a function of  $NH_3$  etching time.

### 3.2 Etching of In-rich $CuInSe_2$ powder

The results of XPS analysis of chemically treated surface composition are summarized in Table I and the results of solution analyses in Table II.

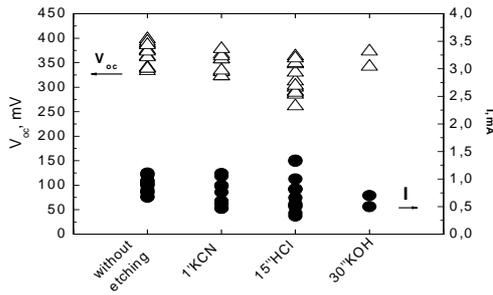
	Virgin (after S-treatment)	KOH-etOH 10 sec.	HCl 15 sec.	KCN 1 min.
Cu	8,5%	9,1%	11,5%	7,5%
In	19,6%	19,8%	13,4%	21,9%
Se	56,6%	54,3%	59,1%	53,7%
S	15,3%	16,8%	16,0%	16,9%

**Table I:** XPS compositional analysis of chemically treated  $CuInSe_2$  monograin powder surfaces

These results show that the surface composition of powder crystals is similar to OVC or a two-phase mixture of  $CuIn_3Se_5$  and  $In_2Se_3$  [11]. The bulk composition of In-rich powder crystals, determined polarographically, was: Cu 23,8%, In 26,1% and Se 50,1%.

	15 sec. HCl, mmole/ml	30 sec. KOH, mmole/ml	1min. KCN, mmole/ml	15min. $NH_3$ , mmole/ml
Cu	no	$1.3 \times 10^{-5}$	$4 \times 10^{-5}$	$6,8 \times 10^{-5}$
In	$2.8 \times 10^{-4}$	$2.2 \times 10^{-5}$	$1.8 \times 10^{-7}$	$3,8 \times 10^{-5}$
Se	no	$1 \times 10^{-5}$	$3.8 \times 10^{-7}$	No

**Table II:** The concentration of elements in leaching solution as determined polarographically

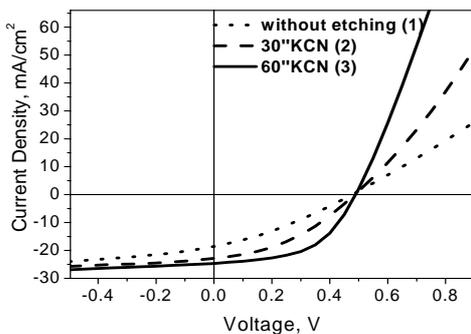


**Figure 4:**  $V_{oc}$  and  $I_{sc}$  of solar cells made on the base of chemically treated In-rich monograin powders

The results of the I-V measurements of solar cells made from chemically treated In-rich materials are presented in Fig. 4. It can be seen that after KOH-EtOH treatment the values of  $I_{sc}$  are a little lower, but the influence of etching is not so destructive as it was in the case of Cu-rich powders. In spite of this, our results confirm that polyurethane-etching time with KOH-EtOH has the crucial influence to the parameters of developed monograin layer solar cells.

The KCN etching is known as a process to remove preferably copper binary phases. Accordingly, treatment of In-rich powders with KCN should not have strong influence on the solar cell performance. Nevertheless, the KCN etching of our In-rich powders before CdS deposition resulted in improved fill factors and currents. The reason for this could be that as our powders passed Se or S vapor treatment before solar cell production, there is possibility that some elemental S or Se had been condensed on crystal surfaces and KCN removed those extra phases [3].

The other possible mechanism for the improvement of solar cell parameters is that the KCN etching depletes Cu sites on crystal surface where Cd adsorption and diffusion occurs [12,13,14]. Cd atoms at Cu sites act as donor defects and, as the result, surface conductivity decreases and even surface conductivity conversion becomes possible [15,16]. Therefore, the interface recombination is decreased. The latter mechanism for solar cell improvement seems to be more likely, because the concentrations of removed Se and In in leaching solution were found to be nearly two orders of magnitude lower than Cu concentration (see data in Table II). Figure 5 shows the current-voltage curves of the monograin layer solar cells with various KCN treatment times.



**Figure 5:** I-V curves of CIS solar cells with different KCN etching times.

HCl etching removes preferably indium from the CIS

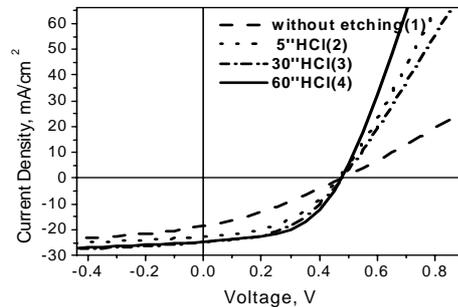
surface. The cells on the base of HCl treated materials showed the higher values of currents, but the lower values of  $V_{oc}$  than the cells on the base of untreated materials. As Cd atoms can reside on both I and III sites [16, 17] then after HCl etching, Cd atoms can reside at removed In sites and act as acceptor defects and thus increase surface conductivity.

Table III gives the maximum measured parameters of various CIS monograin layer solar cells prepared from non-etched and etched materials.

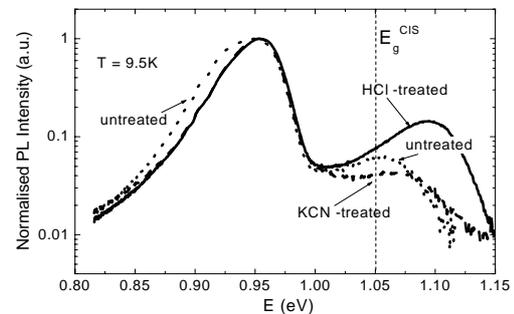
Etching time, etchant	$V_{oc}$ , mV	$J_{sc}$ , mA/cm <sup>2</sup>	FF, %	$\eta$ , %
Without etching	477	18,6	31,3	2,8
30 sec. KCN	486	22,9	39,0	4,3
1 min. KCN	489	24,7	52,6	6,3
5 sec. HCl	465	22,4	45,9	4,8
30 sec. HCl	477	24,8	46,7	5,5
1 min. HCl	473	24,8	51,8	5,9

**Table III:** The performance characteristics of various CuInSe<sub>2</sub> monograin layer solar cells with and without etching.

In comparison with KCN etched samples short time etching with concentrated HCl removes preferably In from the absorber surface (Table II) and leads to the improved values of currents but about 10 mV lower values of open circuit voltages (see Figure 6).



**Figure 6:** I-V curves of CIS solar cells with different HCl etching times



**Figure 7:** PL spectra of treated CuInSe<sub>2</sub> monograin powders.

Fig. 7 shows the PL spectra of CIS powders after different chemical treatments. The measured PL spectra of CIS samples have two broad bands. The first asymmetric band with the maximum around 0.96 eV is the typical spectrum of In-rich CIS. But the PL emission

at higher energies than the bandgap of stoichiometric CuInSe<sub>2</sub> ( $E_g=1.04$  eV) indicates that we have other phases than 1:1:2 in our CIS samples. It can be due to the heat-treatment in sulphur vapour, which causes the formation of a solid solution on the surface. According to [18] this broad band with higher energy is probably originated from CuIn(S<sub>x</sub>Se<sub>1-x</sub>)<sub>2</sub> alloy. But it is also known that CuIn<sub>3</sub>Se<sub>5</sub> and Cu<sub>2</sub>In<sub>4</sub>Se<sub>7</sub> phases have bandgaps higher than CuInSe<sub>2</sub> and usually show PL emission at  $h\nu = 1.05 - 1.1$  eV [19, 20]. Fig. 7 shows that HCl etching results in higher PL peak at  $h\nu = 1.09$  eV. At the same time untreated and KCN treated powders show PL emission at lower energies and can probably originate from the CuIn<sub>3</sub>Se<sub>5</sub> phase.

#### 4 CONCLUSION

The long-time NH<sub>3</sub> etching showed undesirable results to the solar cell performance. KCN etching before CdS deposition resulted in improved solar cell parameters for both type (Cu-rich, In-rich) of materials.

Chemical analysis showed that HCl etching removes preferably In and leaves slightly Se-rich surface. As a result the cells on the base of HCl treated materials showed higher values of currents but lower values of  $V_{oc}$  than these ones without treatment.

Polyurethane-etching time with KOH-EtOH has the crucial influence to the monograin layer solar cell parameters.

Only the combination of above-mentioned chemical treatments before the chemical deposition of CdS leads to the improved parameters of CuInSe<sub>2</sub> monograin layer solar cells.

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#### 6 REFERENCES

[1] J. Kessler, K.O. Velthaus, M. Ruckh, R. Laichinger, H.W. Schock, D. Lincot, R. Ortega, J.Vedel, Proceedings of the PVSEC-6, New Delhi, India, (1992) 1005-1010.  
 [2] T. Delsol, M.C. Simmonds, I.M. Dharmadasa, Solar Energy Materials & Solar Cells 77 (2003) 331-339  
 [3] B. Canava, J. Vigneron, A. Etcheberry, J.F. Guillemoles, D. Lincot, Applied Surface Science 202 (2002) 8-14.  
 [4] T.K. Bandiopadhyay, S.B. Chakraborty, S.R. Chaudhuri, Physica Status Solid A 108 (2) (1988) K119-123.  
 [5] B. Canava, J. Vigneron, A. Etcheberry, D. Guimard, J.F. Guillemoles, D. Lincot, S. Ould Saad Hamatly, Z. Djebbour, D. Mencaraglia, Thin Solid Films 403-404 (2002) 425-431.  
 [6] Y. Okano, T. Nakada, A. Kunioka, Solar Energy Materials and Solar Cells 50 (1998) 105-110.  
 [7] M. Altosaar, E. Mellikov, Jpn. J. Appl. Phys., 39 (2000), Suppl. 39-1, 65-66.

[8] M. Altosaar, A. Jagomägi, M. Kauk, M. Krunks, J. Krustok, E. Mellikov, J. Raudoja, T.Varema, Thin Solid Films 431-432 (2003) 460-469.  
 [9] B.M. Basol, A. Halani, C. Leidholm, G. Norsworthy, V.K. Kapur, A. Swartzlander, R.Matson, Prog. Photovolt. Res. Appl. 8, (2000) 227-235.  
 [10] T. Wada, Y. Hasimoto, K. Kusao, N. Kohara, T. Negami, M. Nishitani, Jap. J.appl. Phys 35 (1996) L1253  
 [11] A.J. Nelson, C.R. Schwerdtfeger, G.C. Herdt, D. King, M. Contreras, K. Ramanathan, W.L. O'Brien, J.Vac. Sci. Technol. A 15 (1997) 2058-2062.  
 [12] T. Wada, S. Hayashi, Y. Hasimoto, Proc. 2<sup>nd</sup> World Conf. Photovoltaic Sol. Energy Conv., Vienna, 1998, p.403-408  
 [13] T. Nakada, Thin Solid Films 361-362 (2000) 346-352.  
 [14] D. Liao, A. Rockett, J. Appl. Phys., 93 (2003) 9380-9382.  
 [15] K. Ramanathan, F.S. Hasoon, S. Smith, D.L. Young, M.A. Contreras, P.K. Johnson, A.O. Pudov, J.R. Sites, J.Phys. Chem. Sol 64 (2003) 1495-1498.  
 [16] T.V. Tavrina, E.I. Rogacheva, J. Phys. Chem. Sol 64 (2003) 1917-1921.  
 [17] P. Fons, K. Sakurai, A. Yamada, K. Matsubara, K. Iwata, T. Baba, Y. Kimura, H.Nakanishi, S. Niki J.Phys. Chem. Sol 64(2003) 1733-1735.  
 [18] A. V. Mudryi, I. A. Victorov, V. F. Gremenok, A. I. Shakin, M. V. Yakushev, Thin Solid Film 431- 432 (2003) 197-199.  
 [19] S. Shirakata, S. Chichibu, H. Miyake, S. Isomura, H. Nakanishi, and K. Sugijama, Inst. Phys. Conf. Ser. No. 152 (1998) 597- 600.  
 [20] Y. Hwang, B. Tseng, Inst. Phys. Conf. Ser. No. 152 (1998) 309- 312.