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## **Oxide nanofilms on silver, copper and their alloys with gold: the kinetics of anodic formation and semiconductor properties**

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## The motivation

The oxide formation strongly depends on the state of the metal/solution interface which is determined by the crystalline structure and chemical composition of the electrode as well as the electrode potential and the solution composition.

The role of Ag crystal face in  $\text{OH}^-$  adsorption and initial stages of  $\text{Ag}_2\text{O}$  growth was revealed [1, 2]. The oxide formation and some structural properties of the oxides on single crystals (111) and (001) of copper were discussed [3].

The role of chemical irregularity of the electrode surface, modeled by the alloying, remains unexamined. Gold is considered the most suitable metal since

- I) Ag-Au as well as Cu-Au system is a continuous series of solid solutions and
- II) gold is thermodynamically stable at the potentials of silver and copper oxide formation.

**The aim** is to reveal the influence of the kinetic features of silver and copper oxide formation, caused by the crystal face of the electrode and its alloying with gold, and some semiconductor properties of the anodic oxide nanofilms.

[1] Droog JMM, J. Electroanal. Chem. 115 (1980) 225

[2] Doubova LM, Daolio S, Pagura C, De Battisti A, Trasatti S, Russ. J. Electrochem. 38 (2002) 20

[3] Kunze J, Maurice V, Klein LH; Strehblow H-H, Marcus P, Cor. Sci. 46 (2004) 245

# Experimental

## The objects

Ag <sub>poly</sub>	Cu <sub>poly</sub>	Deoxygenated 0.1 M KOH
Ag <sub>100</sub> , Ag <sub>110</sub> , Ag <sub>111</sub>		
Ag-Au ( $X_{Au} = 1; 4; 15$ at.%)		
Cu-Au ( $X_{Au} = 4; 15$ at.%)		

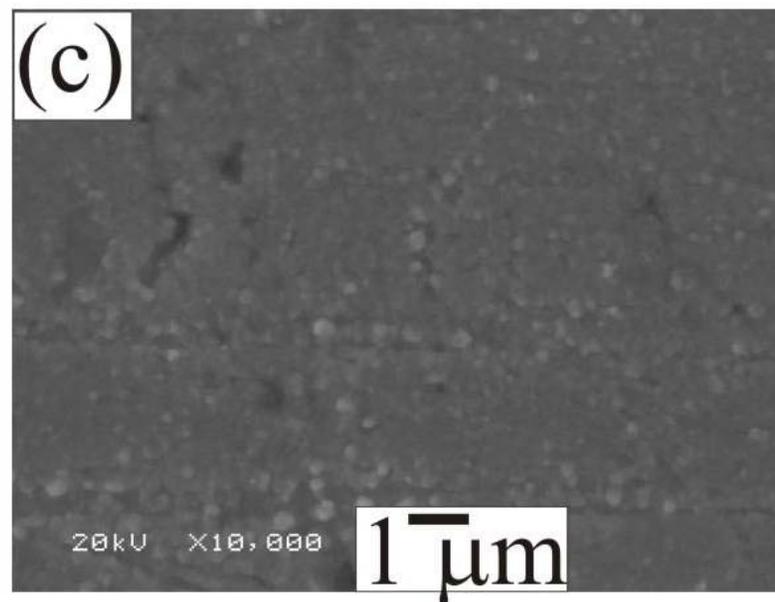
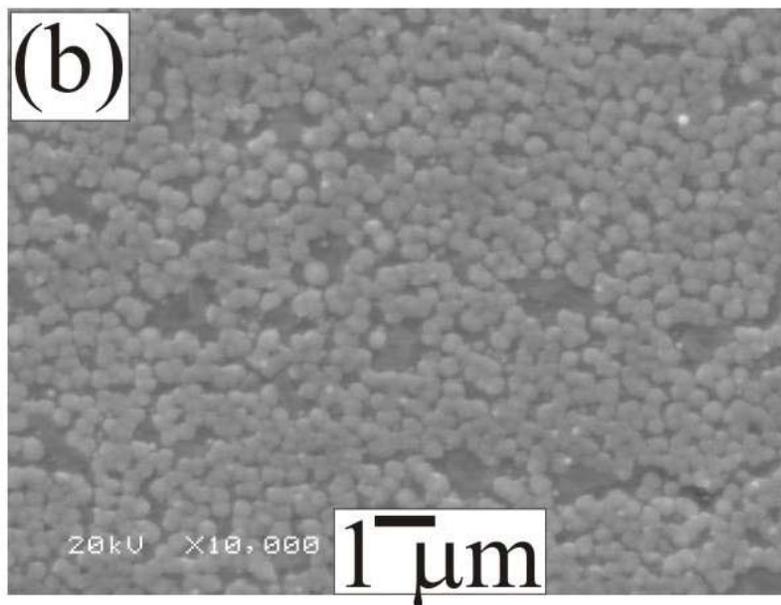
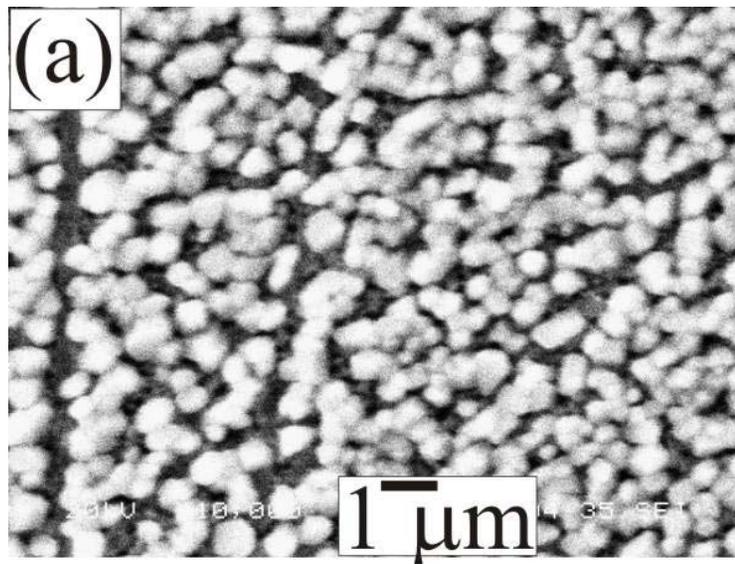
## The parameters of light-emitting diodes (LED)

LED	Parameters		
	Wave length $\lambda$ , nm	Standard angle of divergence, °	Specific light intensity, mWatt cm <sup>-2</sup>
LDUV53393	385	18	1.25
LDUV3333	400	30	3
LSBI3333	430	15	1.5
NSPB300A	470	15	3
NSPE590S	505	10	3
NSPG500S	525	15	2
HLMP-EL08-VY000	592	6	2
HLMP-ED16-UX000	630	15	3.75

## The methods

- Linear voltammetry and chronoammetry (IPC-Compact)
- Photocurrent and photopotential spectroscopy  
(original equipment with a sensibility of 10 nA and 2 ÷ 3  $\mu$ V)
- SEM (JEOL JSM-6380LV)

# SEM- images of $\text{Ag}_2\text{O}$ ( $L = 120 \text{ nm}$ ) on Ag, Ag4Au and Ag15Au



The current efficiency  $\psi / \%$  of  $\text{Ag}_2\text{O}$  formation (nominator)

and the film thickness  $L / \text{nm}$  (denominator)

$q / \text{mC cm}^{-2}$	$E = 0.56 \text{ V}$				Ag1Au $E=0.57 \text{ V}$	Ag4Au $E=0.60 \text{ V}$	Ag15Au $E=0.77 \text{ V}$
	Ag <sub>poly</sub>	Ag <sub>100</sub>	Ag <sub>110</sub>	Ag <sub>111</sub>			
2 ↓	$\frac{71}{2.4}$	$\frac{50}{1.7}$	$\frac{47}{1.6}$	$\frac{60}{2.0}$	$\frac{33}{1.1}$	$\frac{45}{1.5}$	$\frac{40}{1.3}$
3	$\frac{73}{3.7}$	$\frac{58}{2.9}$	$\frac{56}{2.8}$	$\frac{70}{3.5}$	$\frac{41}{2.1}$	$\frac{64}{3.2}$	$\frac{47}{2.4}$
4	$\frac{79}{5.3}$	$\frac{76}{5.1}$	$\frac{63}{4.2}$	$\frac{76}{5.1}$	$\frac{60}{4.0}$	$\frac{65}{4.4}$	$\frac{46}{3.1}$
5	$\frac{83}{6.7}$	$\frac{89}{7.5}$	$\frac{69}{5.8}$	$\frac{82}{6.9}$	$\frac{65}{5.5}$	$\frac{66}{5.6}$	$\frac{58}{4.9}$
7	$\frac{85}{10.0}$	$\frac{90}{10.6}$	$\frac{77}{9.1}$	$\frac{83}{9.8}$	$\frac{72}{8.5}$	$\frac{70}{8.2}$	$\frac{64}{7.5}$

# Photocurrent and photopotential – thin films ( $L < W$ )

$$i_{ph} = i - i_{dark} = e \left[ j_n(x) \Big|_{x=0} - j_p(x) \Big|_{x=0} \right]$$

$E_{ph}$  is calculated under condition of  $i_{ph}=0$

$$i_{ph} = e\eta f\Phi_0 (1 - R_{ref}^{out}) (1 - e^{-2\alpha L}) = i_{ph}^{max} (1 - e^{-2\alpha L}) \approx 2\alpha i_{ph}^{max} L$$

$$E_{ph} = -\frac{2kT}{e} \cdot \frac{\eta f\Phi_0 (1 - R_{ref}^{out}) \alpha L^2}{N_D D_n} e^{\frac{e(E - E_{fb})}{kT}}$$

Assumptions:

$$R_{ref}^{inn} \approx 1$$

$$L / \sqrt{2} L_D < 1$$

$\eta$  – quantum efficiency

$f$  – coefficient of holes assimilation at the outer interface in electrochemical reaction

$\Phi_0$  – light intensity

$R_{ref}^{out}$  – coefficient of reflection from the outer interface

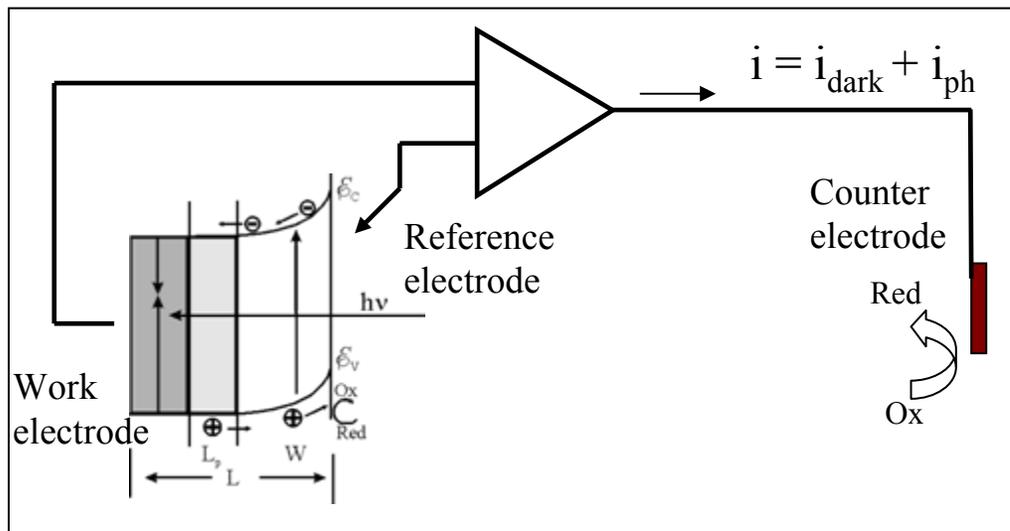
$\alpha$  – coefficient of light absorption

$N_D$  – concentration of donor defects

$D_n$  – coefficient of electron diffusion

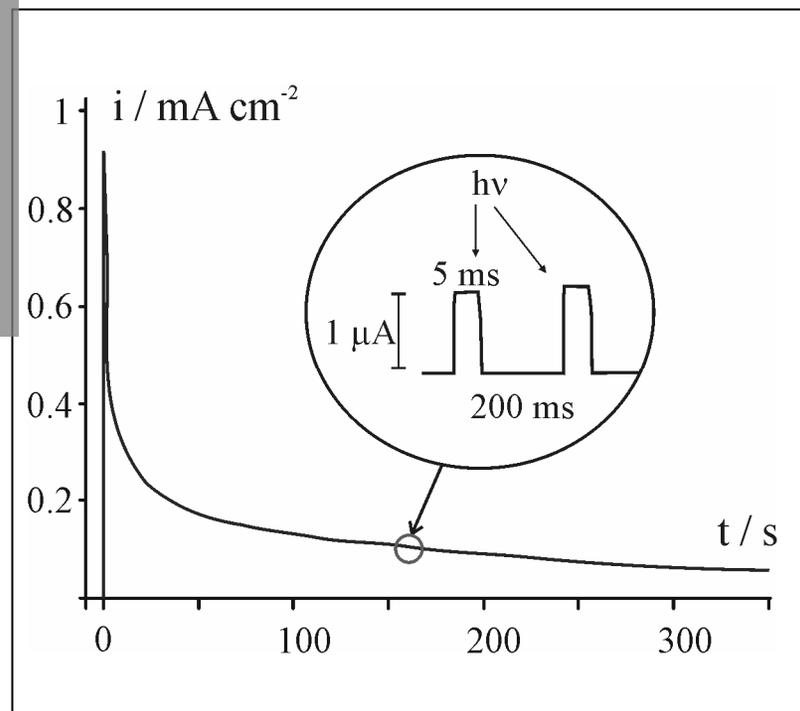
$E_{fb}$  – flatband potential

# Photocurrent measurements in chronoammetry of Ag



The scheme of photocurrent registration

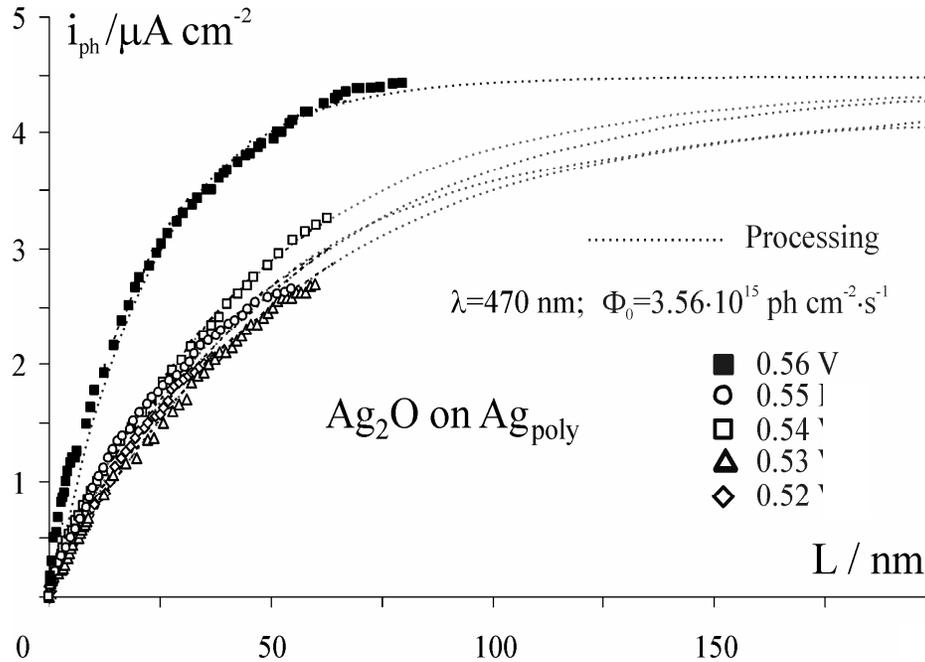
$L$  – film thickness  
 $W$  – space charge region  
 $L_D$  – Debye's length



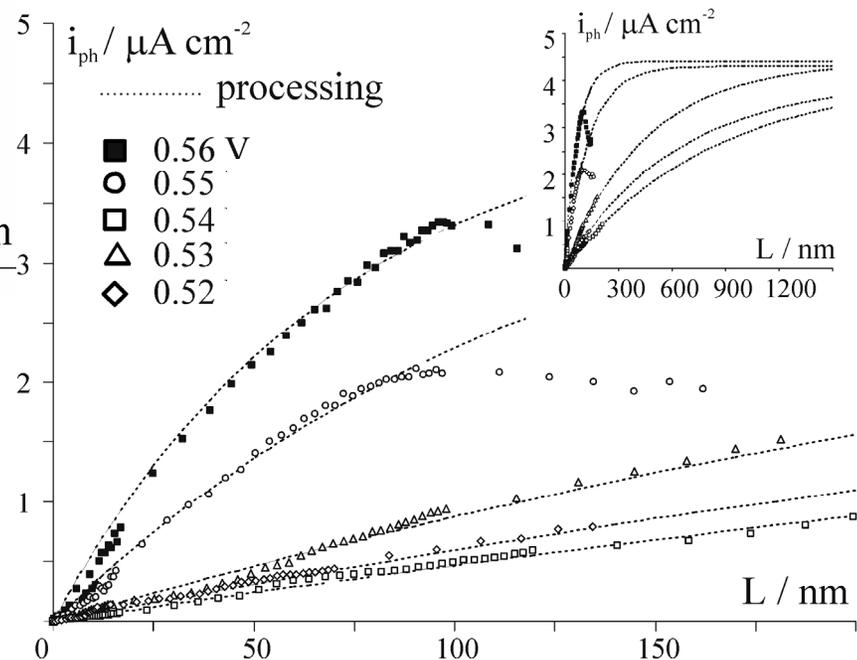
Chronoammogram of  $\text{Ag}_{\text{poly}}$  at  $E=0.56$  V and photocurrent

# The growth of photocurrent with film thickness

$$i_{\text{ph}} = e\Phi_0\eta f(1 - R_{\text{ref}}^{\text{out}}) \cdot (1 - e^{-2\alpha L}) = i_{\text{ph}}^{\text{max}} (1 - e^{-2\alpha L}) \approx 2\alpha i_{\text{ph}}^{\text{max}} L \quad (L < W)$$



The dependence of photocurrent  
( $\lambda = 470 \text{ nm}$ ,  $\Phi_0 = 3.56 \cdot 10^{15} \text{ photon cm}^{-2} \text{ s}^{-1}$ )  
on  $\text{Ag}_2\text{O}$  film thickness



## Structural and optical parameters of $\text{Ag}_2\text{O}$ at different potentials of film

formation on polycrystalline Ag ( $\lambda=470$  nm;  $\Phi_0=3.56 \cdot 10^{15}$  photon  $\text{cm}^{-2} \text{s}^{-1}$ )

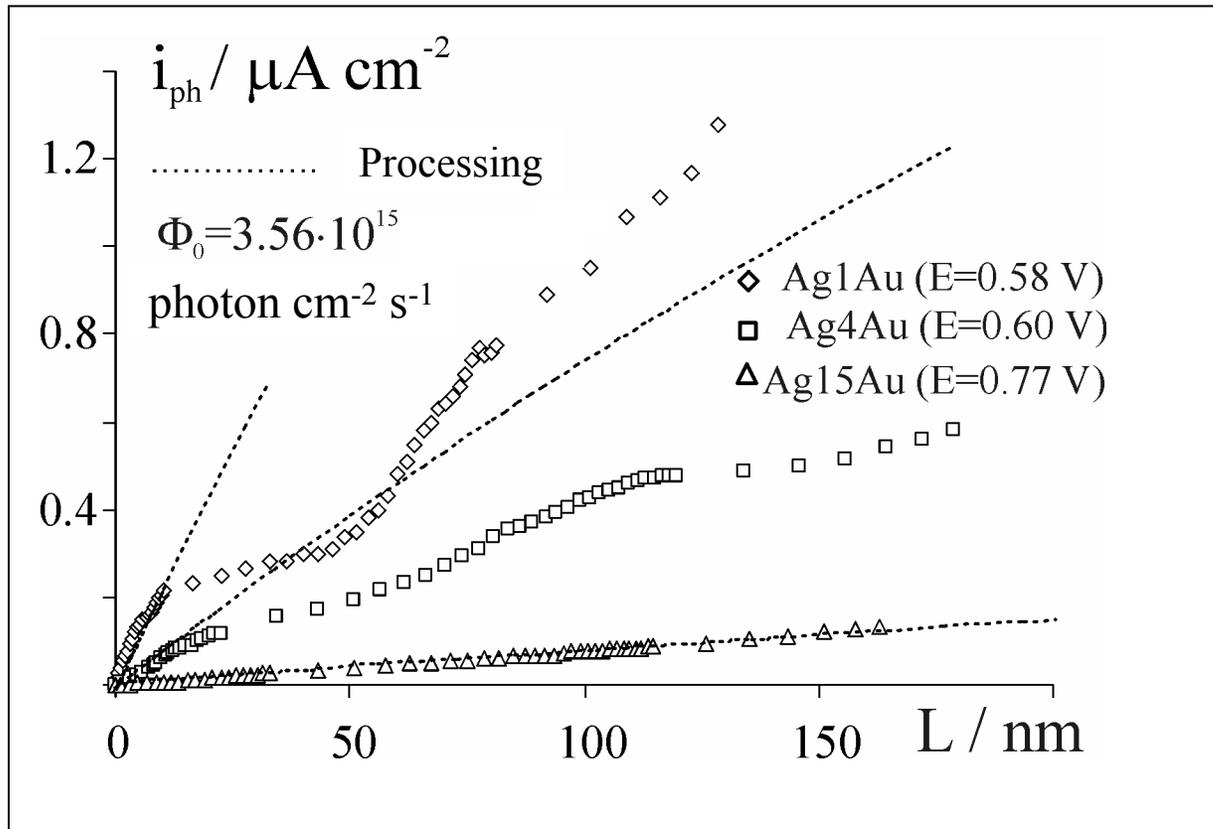
$E / \text{V}$	0.52	0.53	0.54	0.55	0.56
$i_{\text{ph}}^{\text{max}} / \mu\text{A cm}^{-2}$	4.4	4.2	4.3	4.0	4.4
$\eta f(1 - R_{\text{ref}}^{\text{out}}) \cdot 10^4$	77	73	75	70	77
$\alpha \cdot 10^{-5} / \text{cm}^{-1}$	0.90	0.90	1.08	1.10	2.30
$\alpha^{-1} / \text{nm}$	111	111	93	91	44
$W / \text{nm}$	256	256	213	209	100
$N_{\text{D}} \cdot 10^{-15} / \text{cm}^{-3}$	2.83	2.98	4.51	4.90	22.40
$L_{\text{D}} / \text{nm}$	74.3	72.5	58.9	56.5	26.4
$\alpha L_{\text{D}}$	0.67	0.65	0.63	0.62	0.61

$W (\text{Ag}_2\text{O on Ag}_{\text{hkl}}) \gg W (\text{Ag}_2\text{O on Ag}_{\text{poly}})$

$N_{\text{D}} (\text{Ag}_2\text{O on Ag}_{\text{hkl}}) \ll N_{\text{D}} (\text{Ag}_2\text{O on Ag}_{\text{poly}})$

Hence, more stoichiometric oxide is formed on silver single crystals.

# Photocurrent in $\text{Ag}_2\text{O}$ on Ag-Au alloys



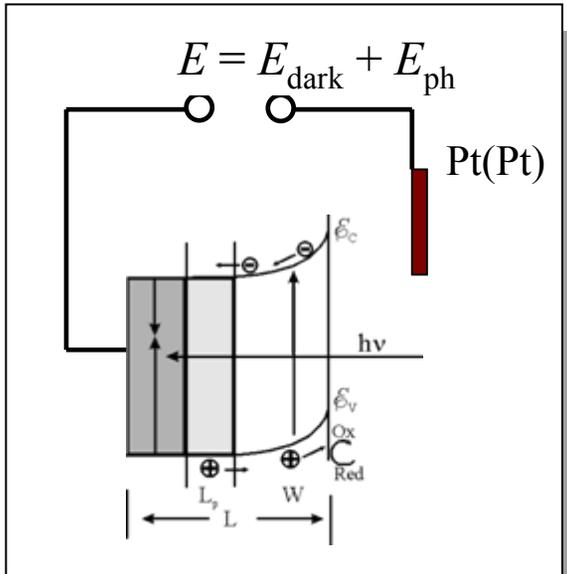
The dependence of photocurrent on  $\text{Ag}_2\text{O}$  thickness

Optical and structural parameters of  $\text{Ag}_2\text{O}$  on Ag-Au alloys

$X_{\text{Au}} / \text{at.}\%$	$E / \text{V}$	$\alpha \cdot 10^{-5} / \text{cm}^{-1}$	$W / \text{nm}$	$N_{\text{D}} \cdot 10^{-12} / \text{cm}^{-3}$	$\eta f(1 - R_{\text{ref}}^{\text{out}}) \cdot 10^4$	$L_{\text{D}} / \text{nm}$	$\alpha L_{\text{D}}$
1	0.58	0.3	767	414	70	194	0.58
4	0.6	0.1	2300	49.7	72	570	0.57
15	0.77	0.009	25556	0.66	72	4870	0.44

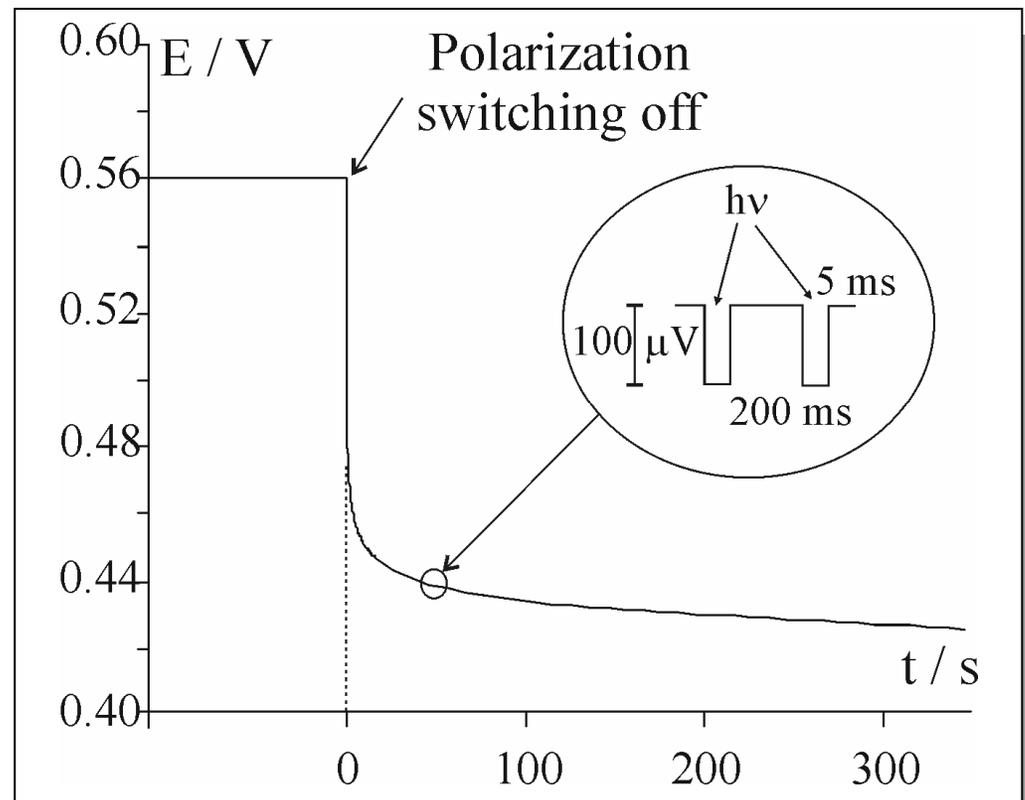
# Photopotential measurements after switching off the polarization

The scheme of photopotential registration

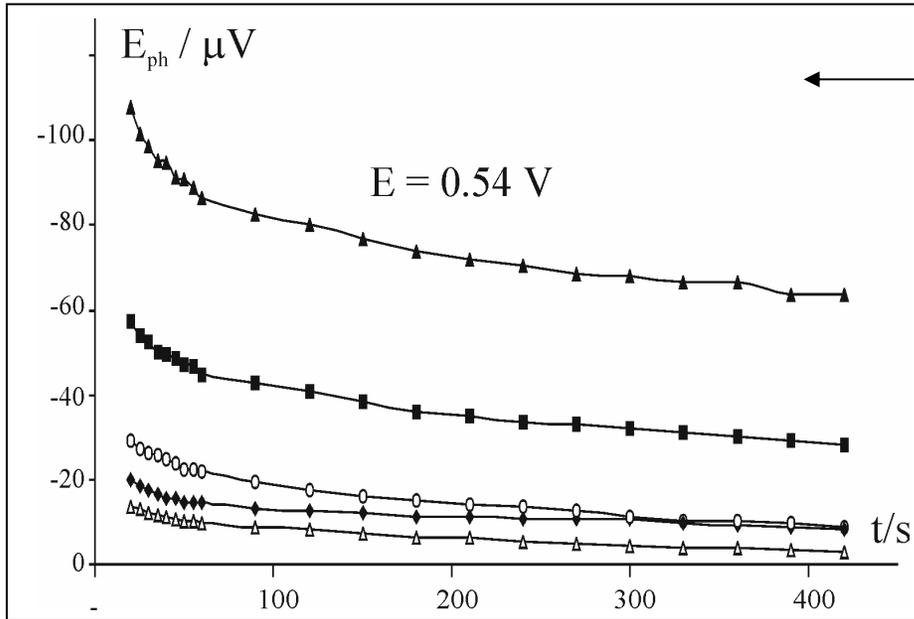


$L$  – the film thickness  
 $W$  – space charge region  
 $L_D$  – Debye's length

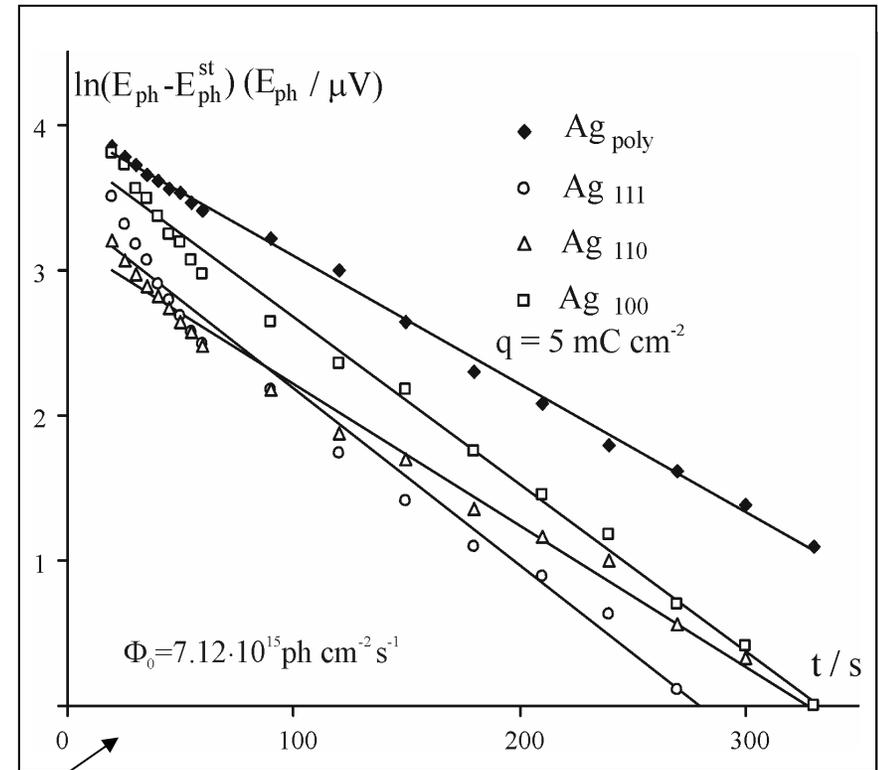
Chronopotentiogram of  $\text{Ag}_{\text{poly}}$  in 0.1 M KOH  
 $q = 7 \text{ mC cm}^{-2}$ ,  $\lambda = 470 \text{ nm}$ ,  $\Phi_0 = 3.56 \cdot 10^{15} \text{ photon cm}^{-2} \text{ s}^{-1}$



# Photopotential – time dependence (after the polarization switching off)



in  $\text{Ag}_2\text{O}$  formed on  $\text{Ag}_{\text{poly}}$ ;  
 $q = 2(\Delta), 3(\blacklozenge), 4(o), 5(\blacksquare), 7(\blacktriangle) \text{ mC cm}^{-2}$



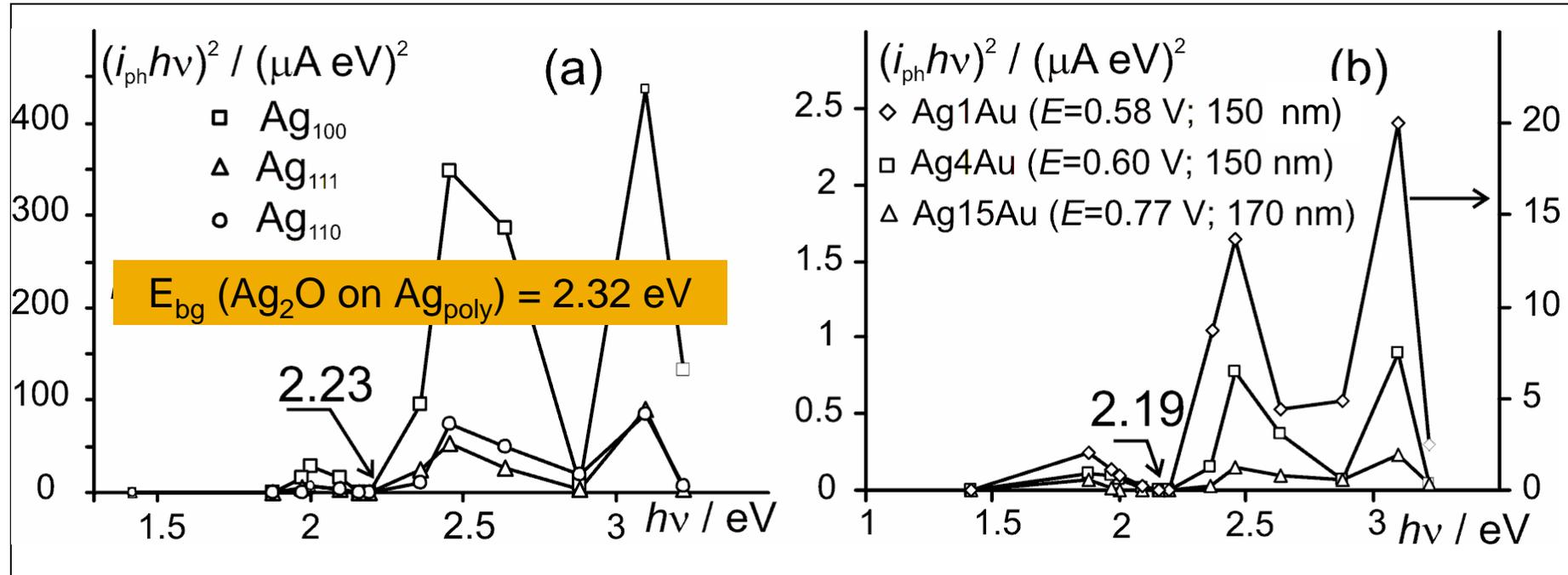
$$\ln [E_{ph}(t) - E_{ph}^{st}] = \ln [E_{ph}(0) - E_{ph}^{st}] - \vec{k}t$$

in  $\text{Ag}_2\text{O}$  formed on  $\text{Ag}_{\text{poly}}$  and  
 single crystals;  $q = 5 \text{ mC cm}^{-2}$

# Photocurrent spectroscopy

$$(i_{\text{ph}} h\nu)^{2/m} = C_1 L^{2/m} (h\nu - \mathcal{E}_{\text{bg}})$$

$C_1$  and  $C_2$  are the constants,  
the parameter  $m$  is equal to 1 or 4 for direct or indirect optical transition respectively



The estimation of band gap of  $\text{Ag}_2\text{O}$  for direct transitions

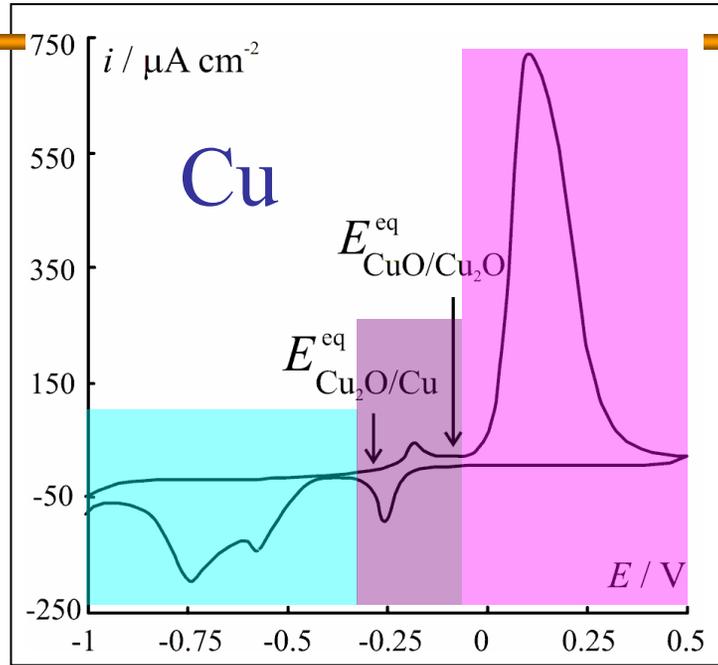
## The parameters of Ag(I) oxide

formed at  $E = 0.56$  V on different substrates

Parameter		Electrode system		
		$\text{Ag}_2\text{O} \text{Ag}_{\text{poly}}$	$\text{Ag}_2\text{O} \text{Ag}_{\text{hkl}}$	$\text{Ag}_2\text{O} \text{Ag-Au}$
$\alpha / \text{cm}^{-1}$		2.3	0.7÷1.4	0.001÷0.1
$W / \text{nm}$		100	164÷330	767÷2300
$L_D / \text{nm}$		26	43÷87	194÷570
$\alpha L_D$		0.61	0.60÷0.61	0.57÷0.58
$\eta f(1 - R_{\text{ref}}^{\text{out}}) \cdot 10^4$		77	75÷79	70÷72
$N_D \cdot 10^{15} / \text{cm}^{-3}$		22.4	2.1÷8.3	0.05÷0.4
$\mathcal{E}_{\text{bg}}^{\text{direct}} / \text{eV}$	on $i_{\text{ph}}$ data	2.32	2.23	2.19
	on $E_{\text{ph}}$ data	2.09	2.09	-

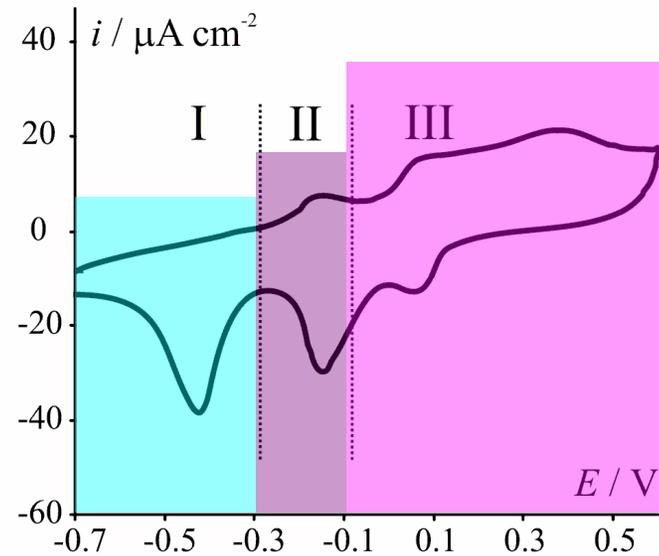
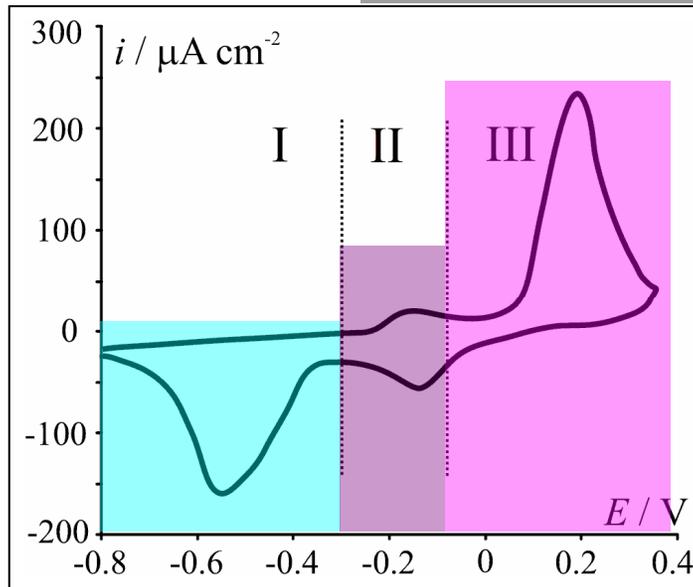
# Electrochemical investigation on Cu and Cu-Au in 0.1 KOH

$$dE/dt = 1 \text{ mV s}^{-1}$$



**Cu<sub>4</sub>Au**

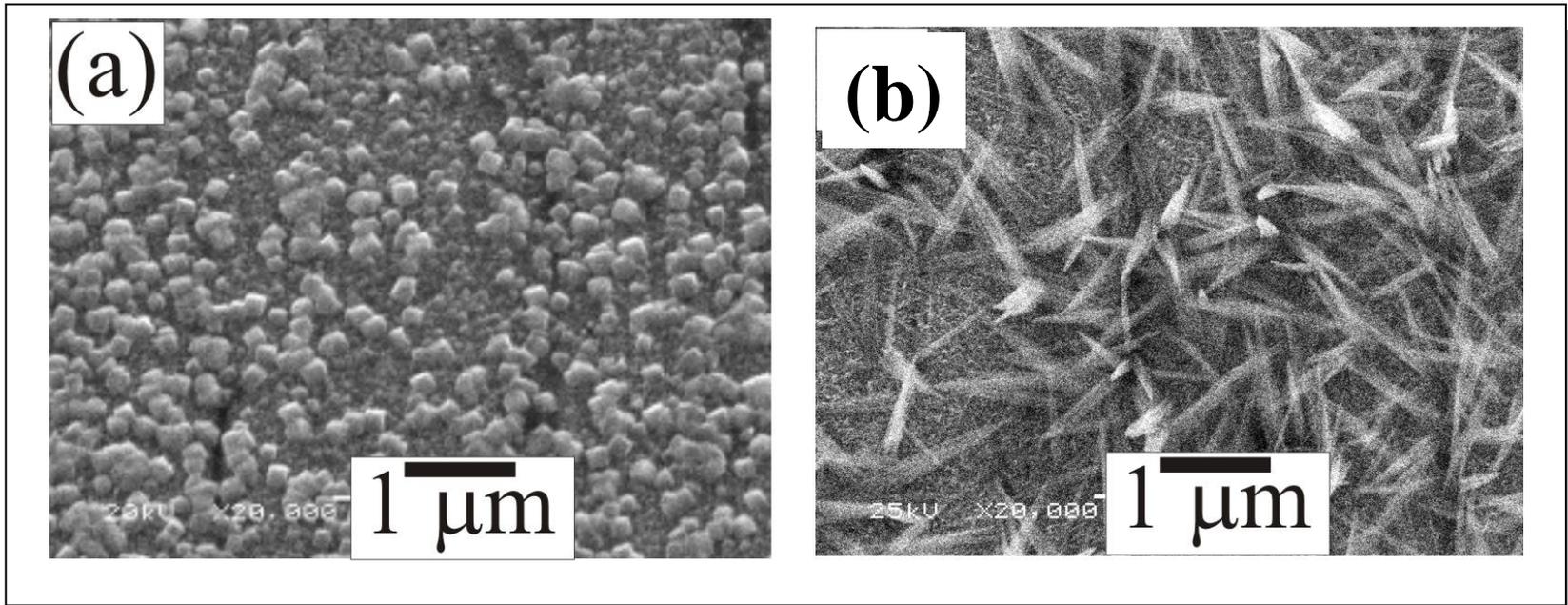
**Cu<sub>15</sub>Au**



## SEM-images of $\text{Cu}_2\text{O}$ and $\text{CuO}$ formed on $\text{Cu}_{\text{poly}}$

(a)  $E = -0.19 \text{ V}$  ( $t = 60 \text{ min}$ ,  $L = 16 \text{ nm}$ )

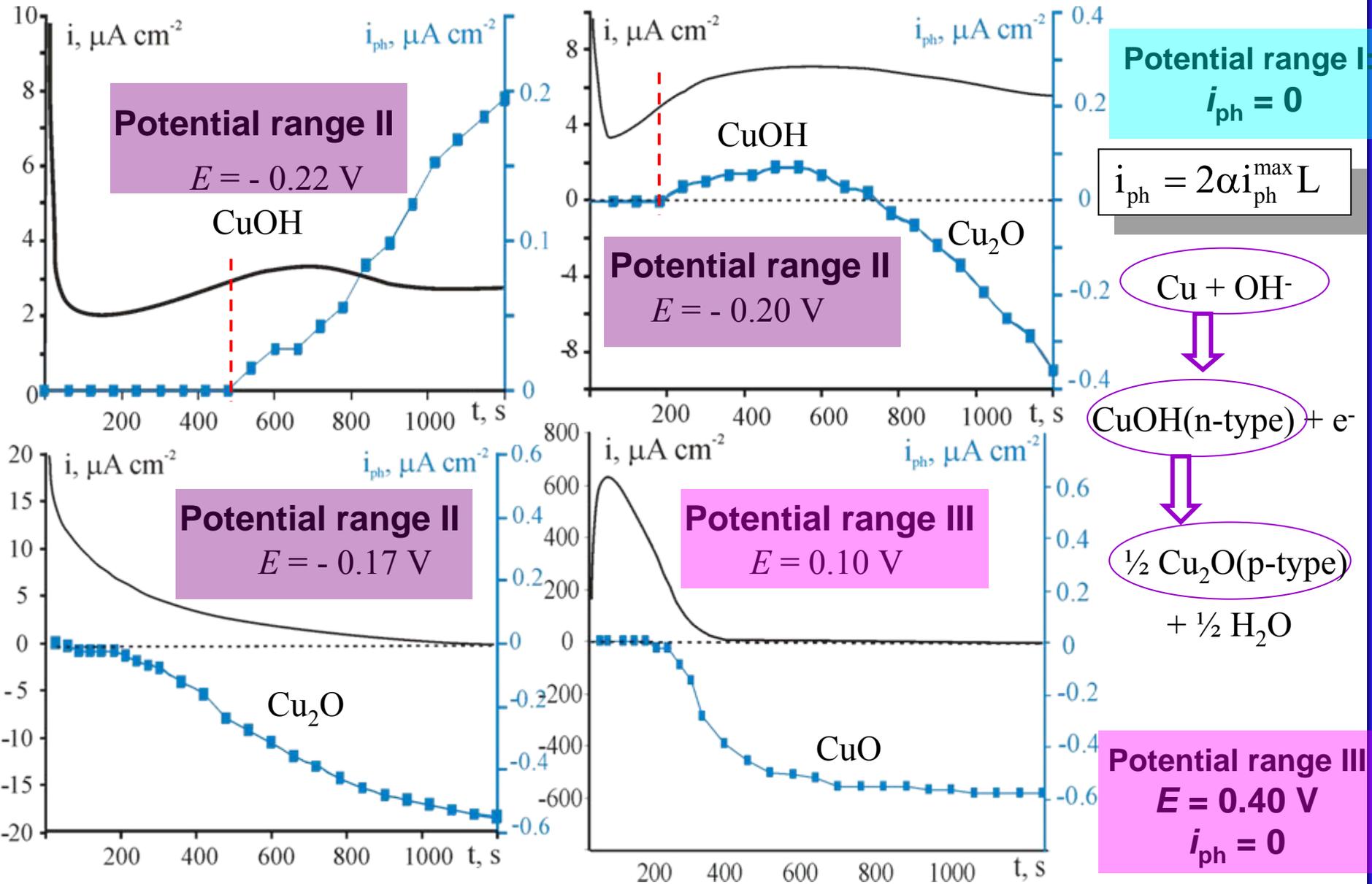
(b)  $E = 0.10 \text{ V}$  ( $t = 15 \text{ min}$ ,  $L = 40 \text{ nm}$ )



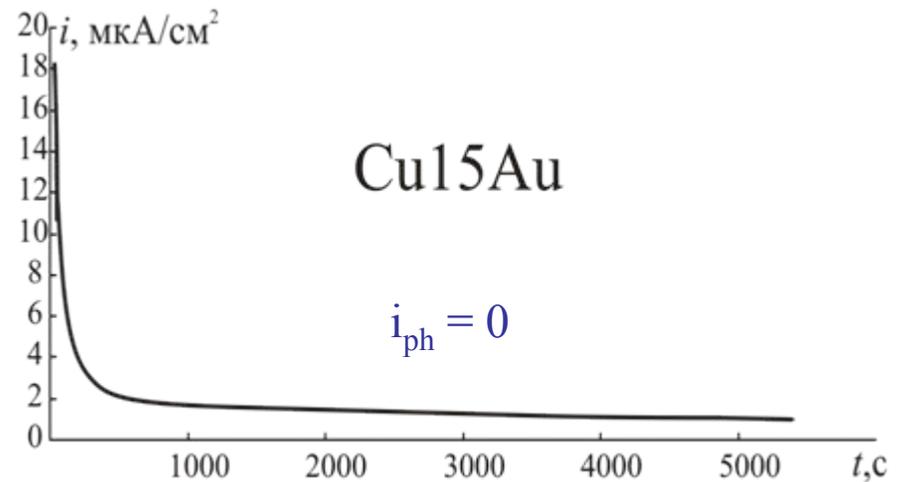
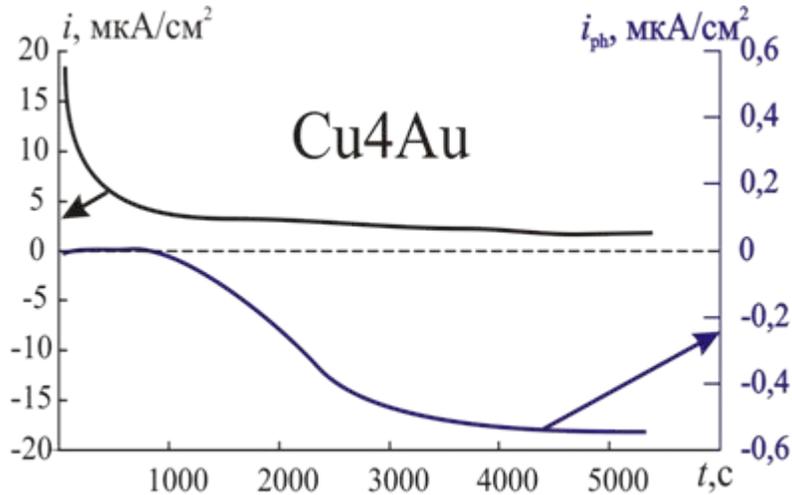
The current efficiency  $\psi / \%$  of the oxide formation on Cu and Cu-Au

The electrode	Cu	Cu4Au	Cu15Au
The range II ( $\text{Cu}_2\text{O}$ formation)	~100	~100	~100
The range III ( $\text{CuO}$ formation)	62	85	57

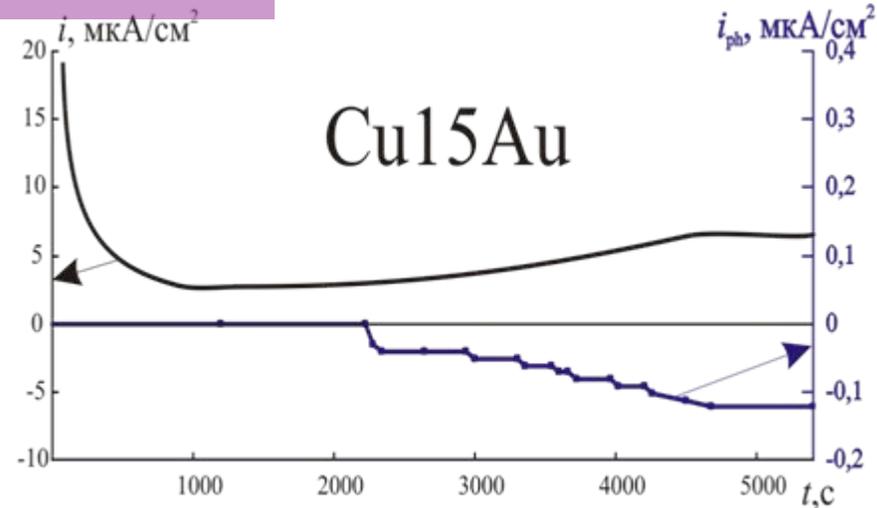
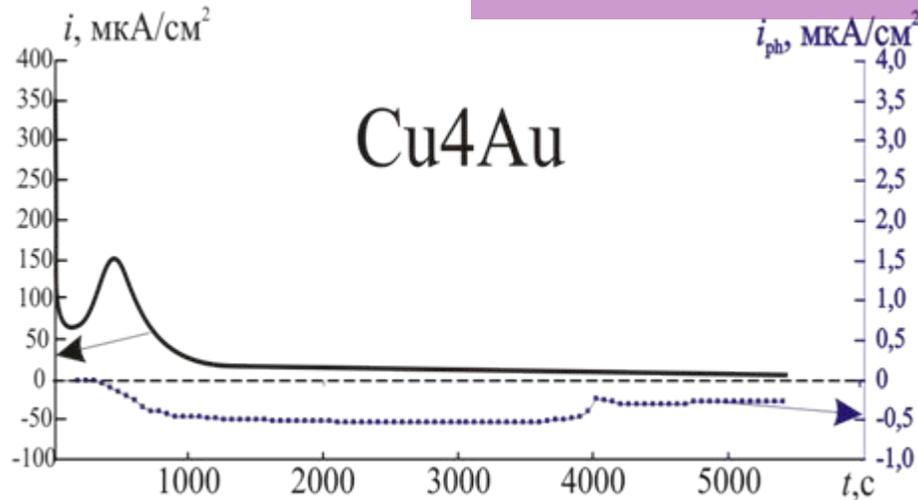
# Photocurrent measurements on copper



# Photocurrent measurements on Cu-Au



$E = -0.1$  V (potential range II)

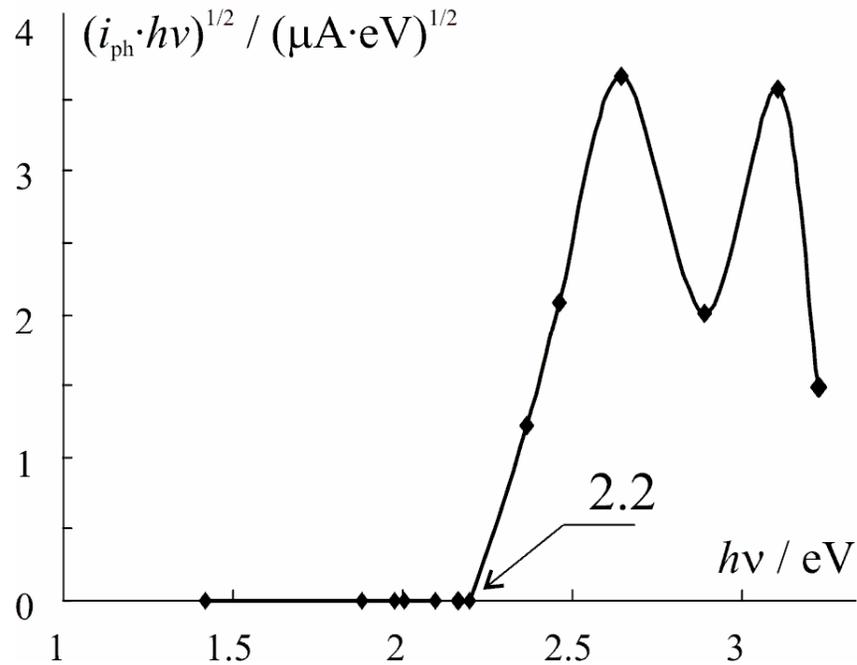


$E = 0.1$  V (potential range III)

# Photocurrent spectroscopy

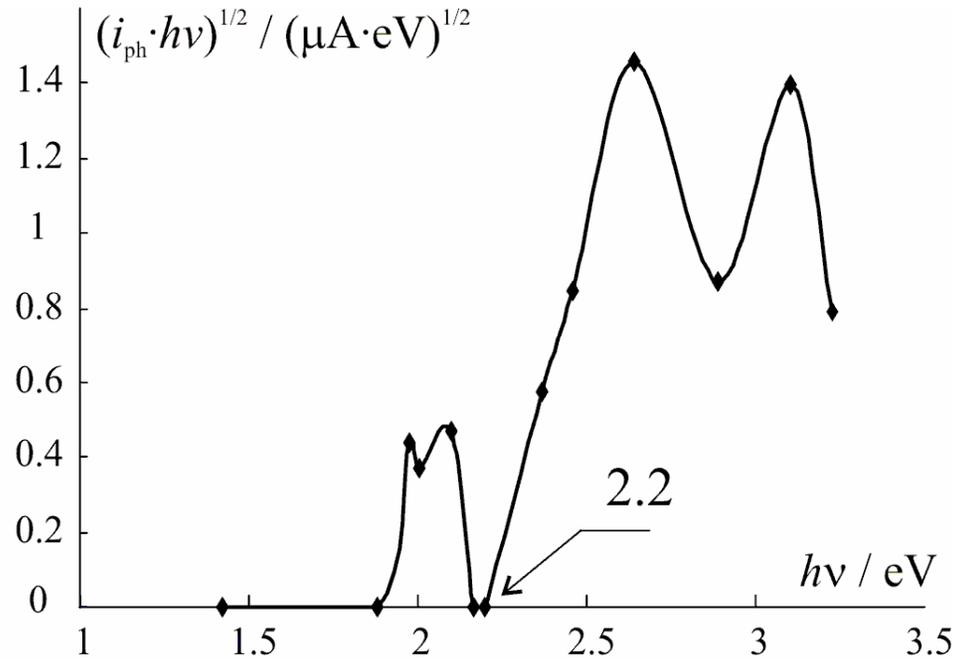
$$(i_{\text{ph}} h\nu)^{2/m} = C_1 L^{2/m} (h\nu - \mathcal{E}_{\text{bg}})$$

$C_1$  is a constants, the parameter  $m = 4$  for indirect optical transition



$\text{Cu}_2\text{O}$  formation

$E = -0.17 \text{ V}$



$\text{Cu}_2\text{O}$  and  $\text{CuO}$  formation

$E = 0.10 \text{ V}$

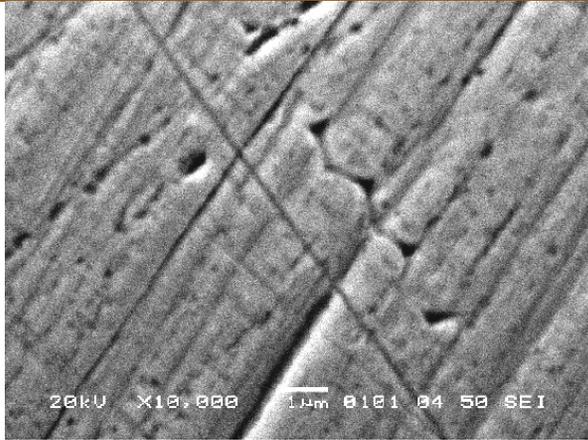
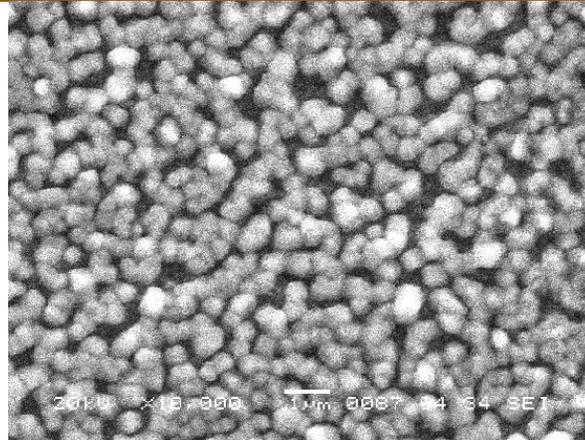
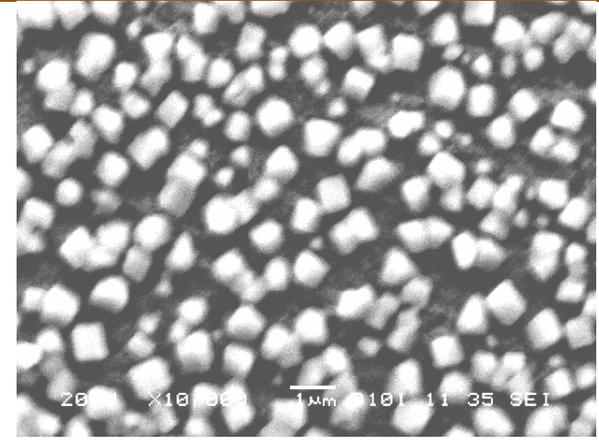
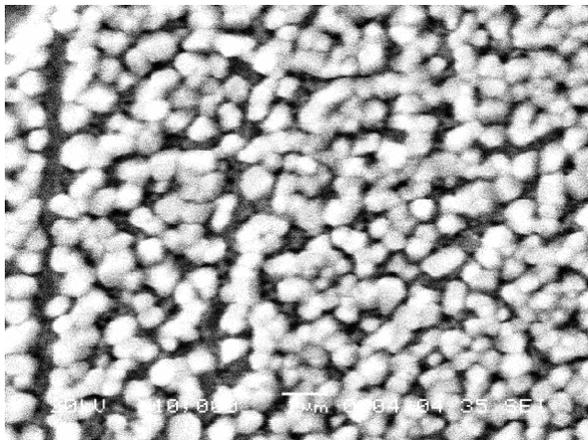
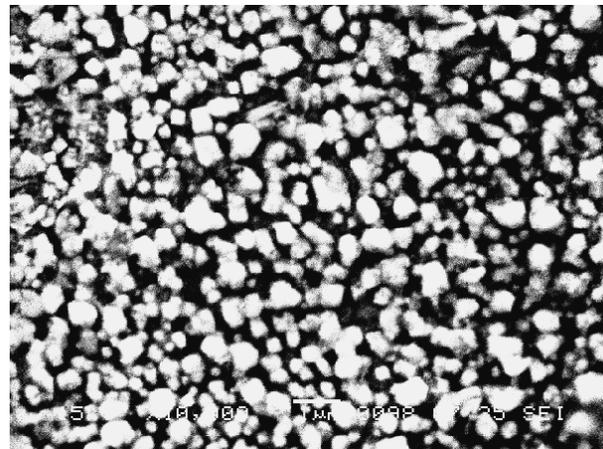
## Conclusions

- The predominant route of Ag(I) oxides anodic formation is not the precipitation from the near-electrode layer, but mainly the direct electrochemical reaction. The thickness of these oxide films does not exceed the space charge region.
- On Ag and Ag-Au alloys n-type Ag(I) oxide with a prevalence of donor defects is formed. The transition from polycrystalline Ag to single crystals as well as the alloying of silver with gold up to 4 at.% results in a decrease of the band gap of Ag<sub>2</sub>O and an increase of the stoichiometry.
- On Cu and Cu-Au alloys the p-type Cu(I) and Cu(II) oxides with a prevalence of acceptor defects are formed. Cu(I) oxide has the band gap of 2.2 eV with the prevalence of indirect optical transitions. At the initial stage of anodic oxidation the oxide layer with n-type conductivity appears. During the thickening the n-type oxide phase transforms into the p-type Cu(I) oxide.
- Copper is subject to corrosion even in a thoroughly deoxygenated solution with Cu<sub>2</sub>O formation. The preliminary anodic formation of a thin Cu(I) oxide as well as the alloying of copper with gold (up to 4 and 15 at.%) hampers this process.

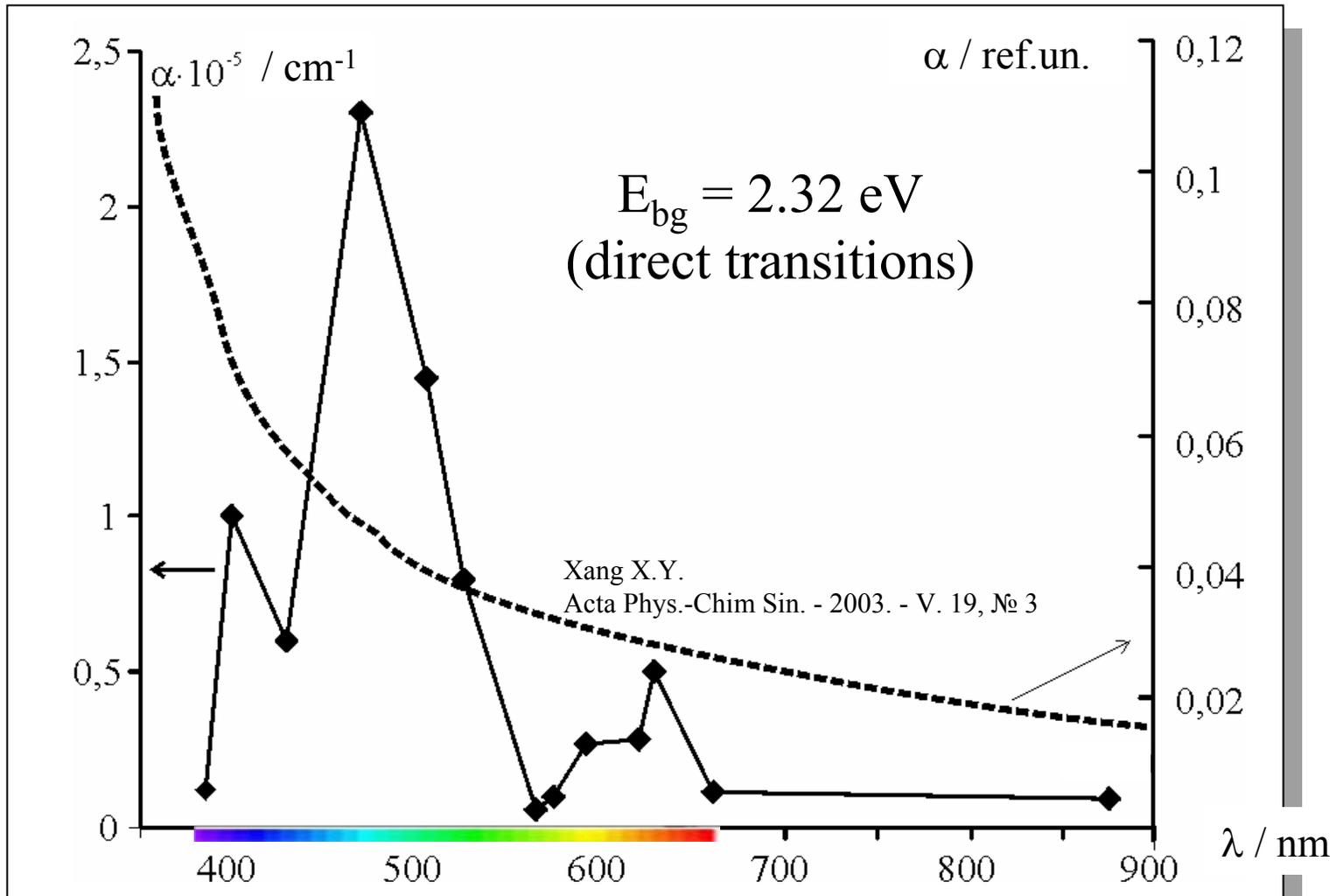
## Acknowledgements

We are grateful for financial supporting to Russian Foundation for Basic Research (09-03-00554a)

## SEM

 $\text{Ag}_{\text{poly}}$  $\text{Ag}_2\text{O}|\text{Ag}_{110}$  $\text{Ag}_2\text{O}|\text{Ag}_{111}$  $\text{Ag}_2\text{O}|\text{Ag}_{\text{poly}}$  $\text{Ag}_2\text{O}|\text{Ag}_{100}$

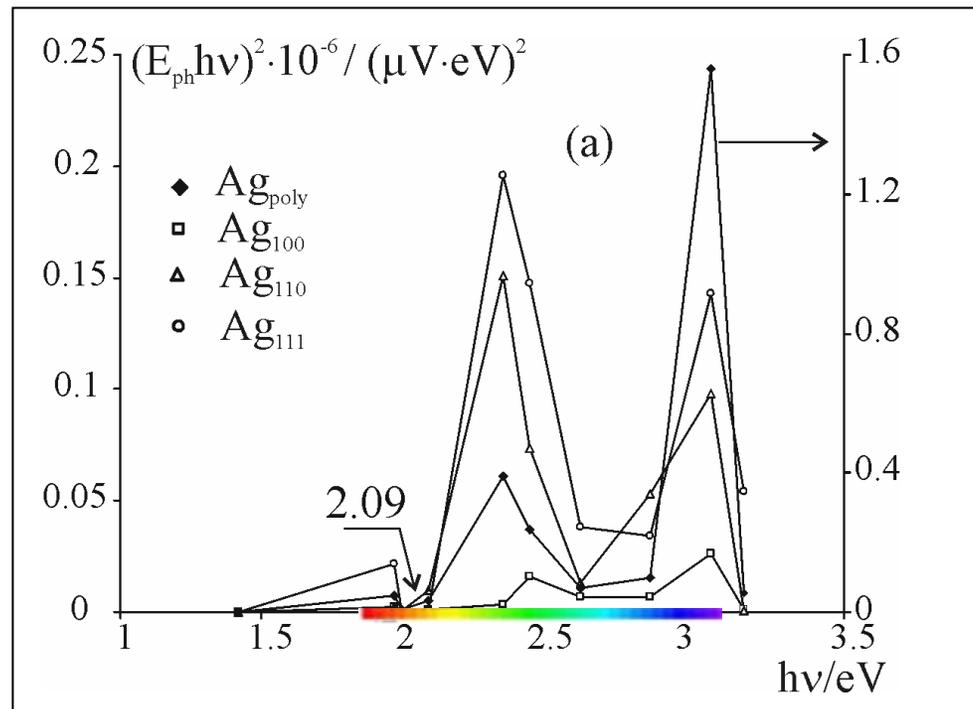
# Photocurrent spectroscopy



Dependence of coefficient of light absorption on the wave length  
 in  $\text{Ag}_2\text{O}$  on  $\text{Ag}_{\text{poly}}$  ( $E=0.56 \text{ V}$ )

# Photopotential spectroscopy

$$\left(E_{\text{ph}} h\nu\right)^{2/m} = C_2 L^{4/m} \left(h\nu - \mathcal{E}_{\text{bg}}\right)$$



The estimation of band gap in  $\text{Ag}_2\text{O}$  for direct transitions

# The role of crystallographic orientation

$E=0.52 \text{ V}$  {

$$\alpha(\text{Ag}_2\text{O}/\text{Ag}_{110}) < \alpha(\text{Ag}_2\text{O}/\text{Ag}_{100}) < \alpha(\text{Ag}_2\text{O}/\text{Ag}_{111})$$

$$N_D(\text{Ag}_2\text{O}/\text{Ag}_{110}) < N_D(\text{Ag}_2\text{O}/\text{Ag}_{100}) < N_D(\text{Ag}_2\text{O}/\text{Ag}_{111})$$

$$W(\text{Ag}_2\text{O}/\text{Ag}_{110}) > W(\text{Ag}_2\text{O}/\text{Ag}_{100}) > W(\text{Ag}_2\text{O}/\text{Ag}_{111})$$

$$L_D(\text{Ag}_2\text{O}/\text{Ag}_{110}) > L_D(\text{Ag}_2\text{O}/\text{Ag}_{100}) > L_D(\text{Ag}_2\text{O}/\text{Ag}_{111})$$

$$[110] < [100] < [111]$$

$E=0.56 \text{ V}$  {

$$\alpha(\text{Ag}_2\text{O}/\text{Ag}_{100}) < \alpha(\text{Ag}_2\text{O}/\text{Ag}_{111}) < \alpha(\text{Ag}_2\text{O}/\text{Ag}_{110})$$

$$N_D(\text{Ag}_2\text{O}/\text{Ag}_{100}) < N_D(\text{Ag}_2\text{O}/\text{Ag}_{111}) < N_D(\text{Ag}_2\text{O}/\text{Ag}_{110})$$

$$W(\text{Ag}_2\text{O}/\text{Ag}_{100}) > W(\text{Ag}_2\text{O}/\text{Ag}_{111}) > W(\text{Ag}_2\text{O}/\text{Ag}_{110})$$

$$L_D(\text{Ag}_2\text{O}/\text{Ag}_{100}) > L_D(\text{Ag}_2\text{O}/\text{Ag}_{111}) > L_D(\text{Ag}_2\text{O}/\text{Ag}_{110}),$$

$$\sigma_n(\text{Ag}_2\text{O}/\text{Ag}_{100}) > \sigma_n(\text{Ag}_2\text{O}/\text{Ag}_{111}) > \sigma_n(\text{Ag}_2\text{O}/\text{Ag}_{110})$$

$$\mu_n(\text{Ag}_2\text{O}/\text{Ag}_{100}) < \mu_n(\text{Ag}_2\text{O}/\text{Ag}_{111}) < \mu_n(\text{Ag}_2\text{O}/\text{Ag}_{110}).$$

# Coulometry

The anodic charge of copper oxidation, the cathodic charge of oxide film reduction and the difference charge of copper corrosion ( $\tau = 10$  minutes)

E, V	-0.7	-0.5	-0.3	-0.2	-0.17	-0.15	-0.12	-0.05	0	0.1
$Q_a = Q_{ox}$ , mC	0	0	0.4	1	1.8	1.7	2.6	3.4	5.4	67.8
$Q_k = Q_{red}$ , mC	9.3	9.0	9.6	6.6	3.3	5.4	8.1	11	9.8	36.6
$Q_k - Q_a = Q_{cor}$ , mC	9.3	9.0	9.2	5.6	1.5	3.7	5.5	7.6	4.4	-

# Photocurrent and photopotential – the theory

## for bulk n-type semiconductor ( $L > W$ )

$$\frac{d}{dx} \left[ \frac{dp(x)}{dx} + p(x) \frac{d\psi(x)}{dx} \right] = -\alpha a_1 e^{-\alpha x} \quad (0 \leq x \leq W)$$

$$\frac{d}{dx} \left[ \frac{dn(x)}{dx} + n(x) \frac{d\psi(x)}{dx} \right] = -\alpha a_2 e^{-\alpha x} \quad (0 \leq x \leq W)$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{e^2}{\epsilon\epsilon_0 kT} \left[ p_0 e^{-\psi(x)} + N_D - n_0 e^{\psi(x)} - N_A \right] \quad (0 \leq x \leq W)$$

$$\psi(x) = \frac{e\phi(x)}{kT} = -\frac{1}{2L_D^2} \begin{cases} (x-W)^2 & L > W \\ (x-L)^2 + (W^2 - L^2) & L < W \end{cases}$$

$$\frac{d^2p(x)}{dx^2} = -\alpha a_1 e^{-\alpha x} + \frac{p(x) - p_0}{L_p^2} \quad (W \leq x \leq L)$$

Assumptions:

- $N_D^+ \approx N_D$
- The volume of semiconductor out of space charge region is quasi-neutral
- Distribution of  $n$  and  $p$  in space charge region in equilibrium state satisfies Boltzmann law
- Recombination during the radiation is negligibly small

$W$  – space charge region

$L$  – film thickness

$L_D$  – Debye's length

$L_p$  – diffusion length

# Photocurrent and photopotential – thin films ( $L < W$ )

with a high level of light absorption ( $\alpha L_D \geq 1$ )

$$i_{\text{ph}} = \eta f \Phi_0 (1 - R_{\text{ref}}^{\text{out}}) (1 + R_{\text{ref}}^{\text{inn}} e^{-\alpha L}) (1 - e^{-\alpha L}) + \frac{e N_D D_n \left(1 - e^{-\frac{e E_{\text{ph}}}{kT}}\right)}{\sqrt{2} L_D \mathcal{F} \left(L / \sqrt{2} L_D\right)} e^{-\frac{e(E - E_{\text{fb}})}{kT}}$$

$$E_{\text{ph}} = -\frac{kT}{e} \ln \left[ 1 + \frac{\eta f \Phi_0 (1 - R_{\text{ref}}^{\text{out}}) (1 - R_{\text{ref}}^{\text{inn}} e^{-\alpha L}) (1 - e^{-\alpha L})}{N_D D_n} L_D \sqrt{2} \mathcal{F} \left( \frac{L}{\sqrt{2} L_D} \right) e^{-\frac{e(E - E_{\text{fb}})}{kT}} \right]$$

$\eta$  – quantum efficiency;  $\Phi_0$  – light intensity

$f$  – coefficient of holes assimilation in electrochemical reactions at the outer interface

$N_D$  – concentration of donor defects;  $D_n$  – coefficient of electron diffusion

$\alpha$  – coefficient of light absorption;  $E_{\text{fb}}$  – flatband potential

$R_{\text{ref}}^{\text{out}}$  and  $R_{\text{ref}}^{\text{inn}}$  – coefficients of reflection from the outer and inner interfaces

$\mathcal{F}(u)$  – integral of Doseon

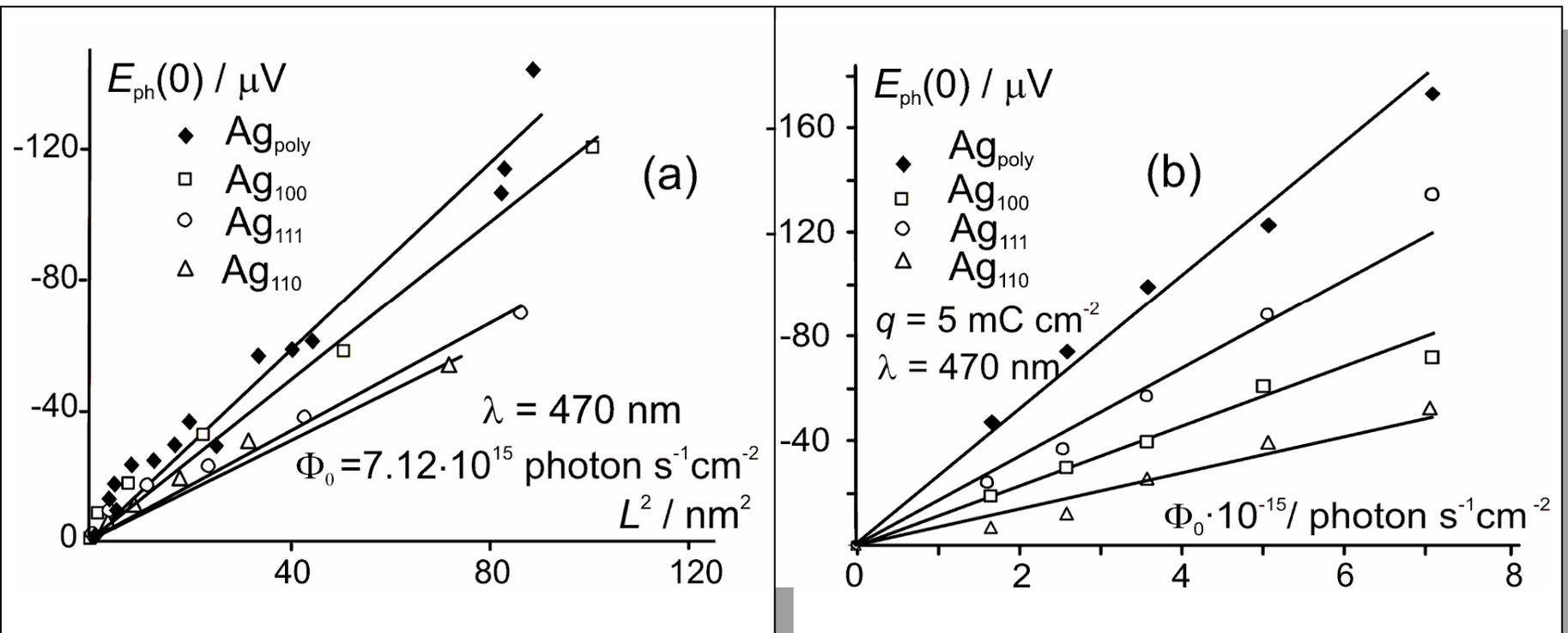
$\mathcal{F}(u) \approx u$  at  $u < 1$

$L < L_D$  hence  $(L / \sqrt{2} L_D) < 1$

and  $\mathcal{F}(L / \sqrt{2} L_D) \approx L / \sqrt{2} L_D$

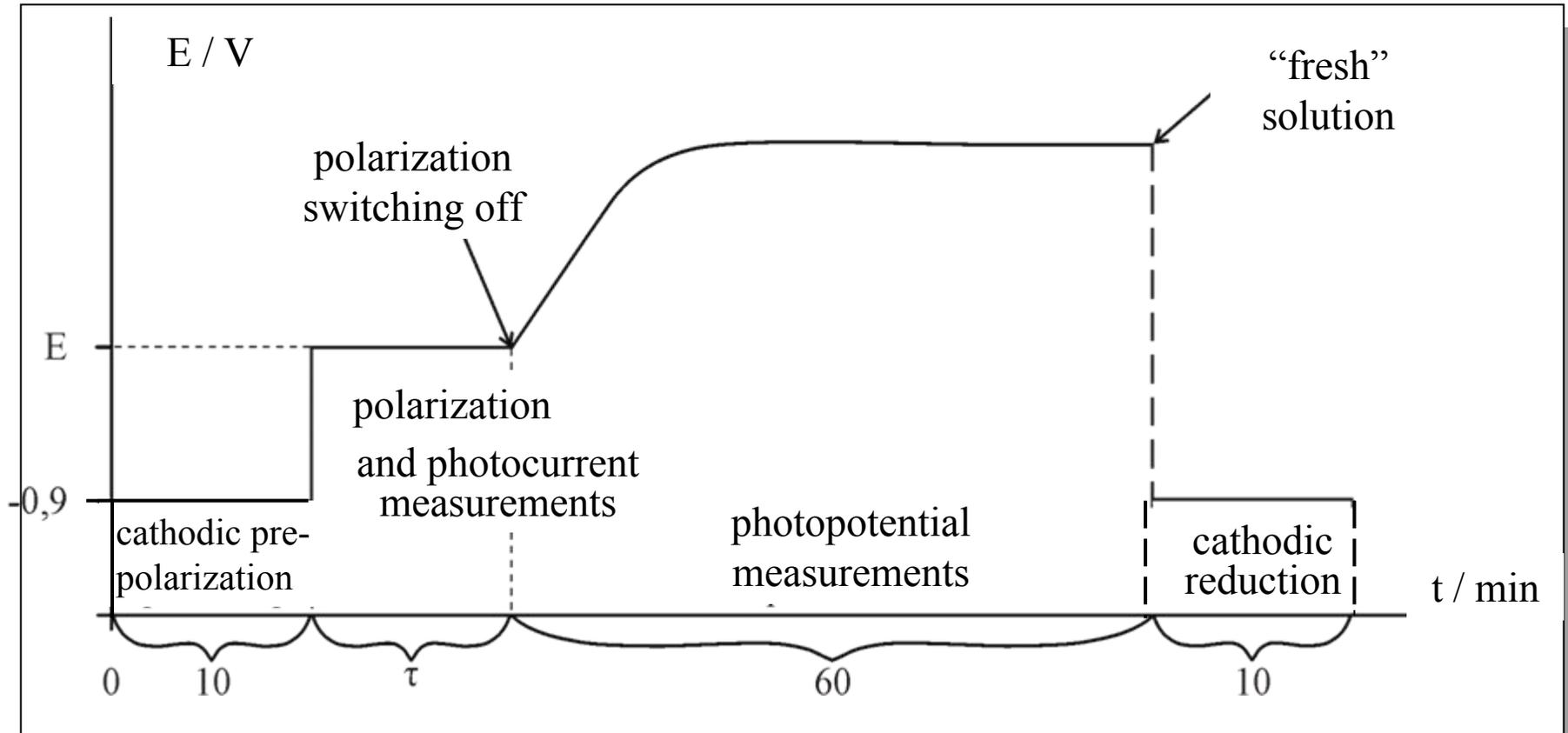
# The dependences of photopotential on film thickness and light intensity

$$E_{\text{ph}} = -\frac{2kT}{e} \cdot \frac{\eta f \Phi_0 (1 - R_{\text{ref}}^{\text{out}}) \alpha L^2}{N_D D_n} e^{\frac{e(E - E_{\text{fb}})}{kT}}$$



The photopotential in  $\text{Ag}_2\text{O}$  formed on  $\text{Ag}_{\text{poly}}$  and  $\text{Ag}_{\text{hkl}}$  at  $E = 0.56 \text{ V}$

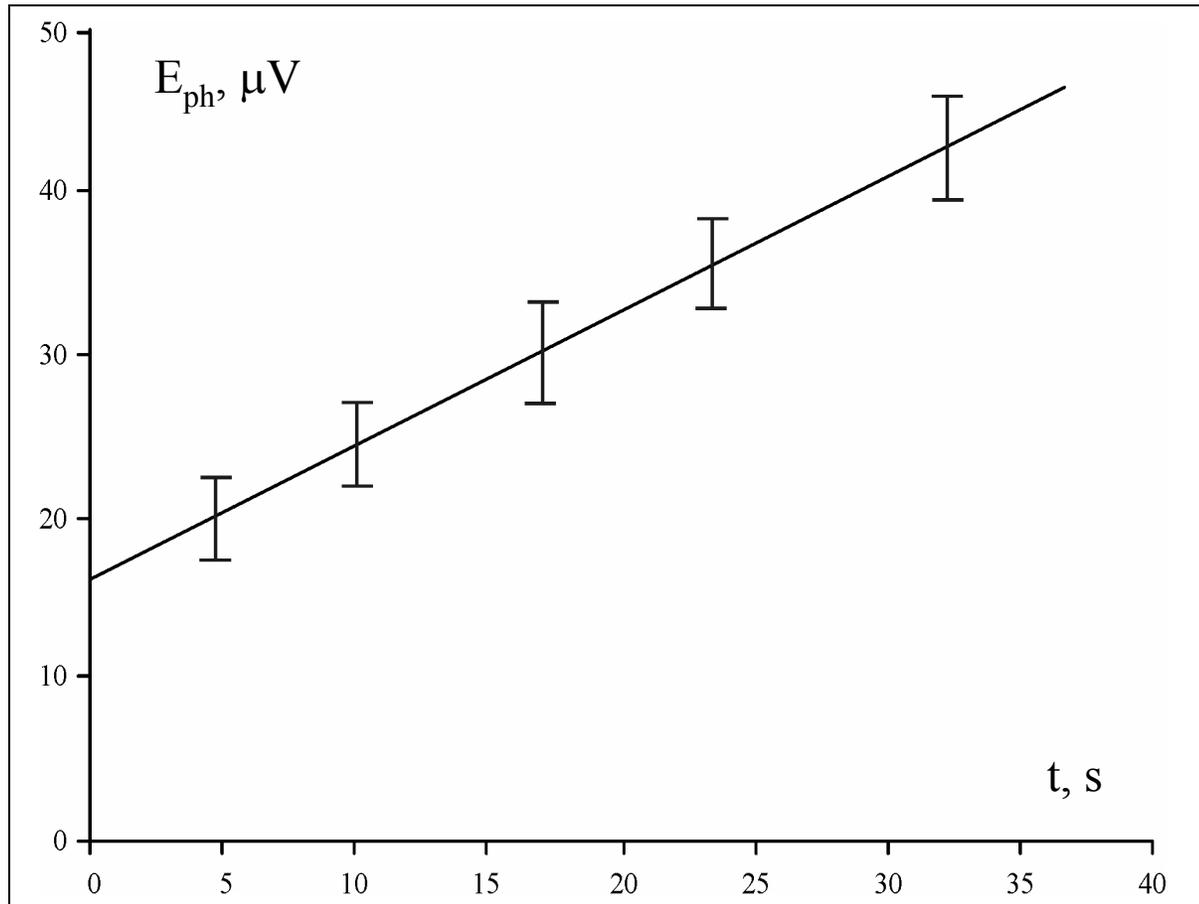
# The scheme of potentiostatic measurements on Cu and Cu-Au



$E = -0.7; -0.5; -0.3; -0.2; -0.15; -0.12; -0.1; -0.05; 0.0; 0.1; 0.2; 0.4$  V (s.h.e.)

$\tau = 10, 15, 20, 25, 30$  minutes

# Photopotential measurements without any polarization



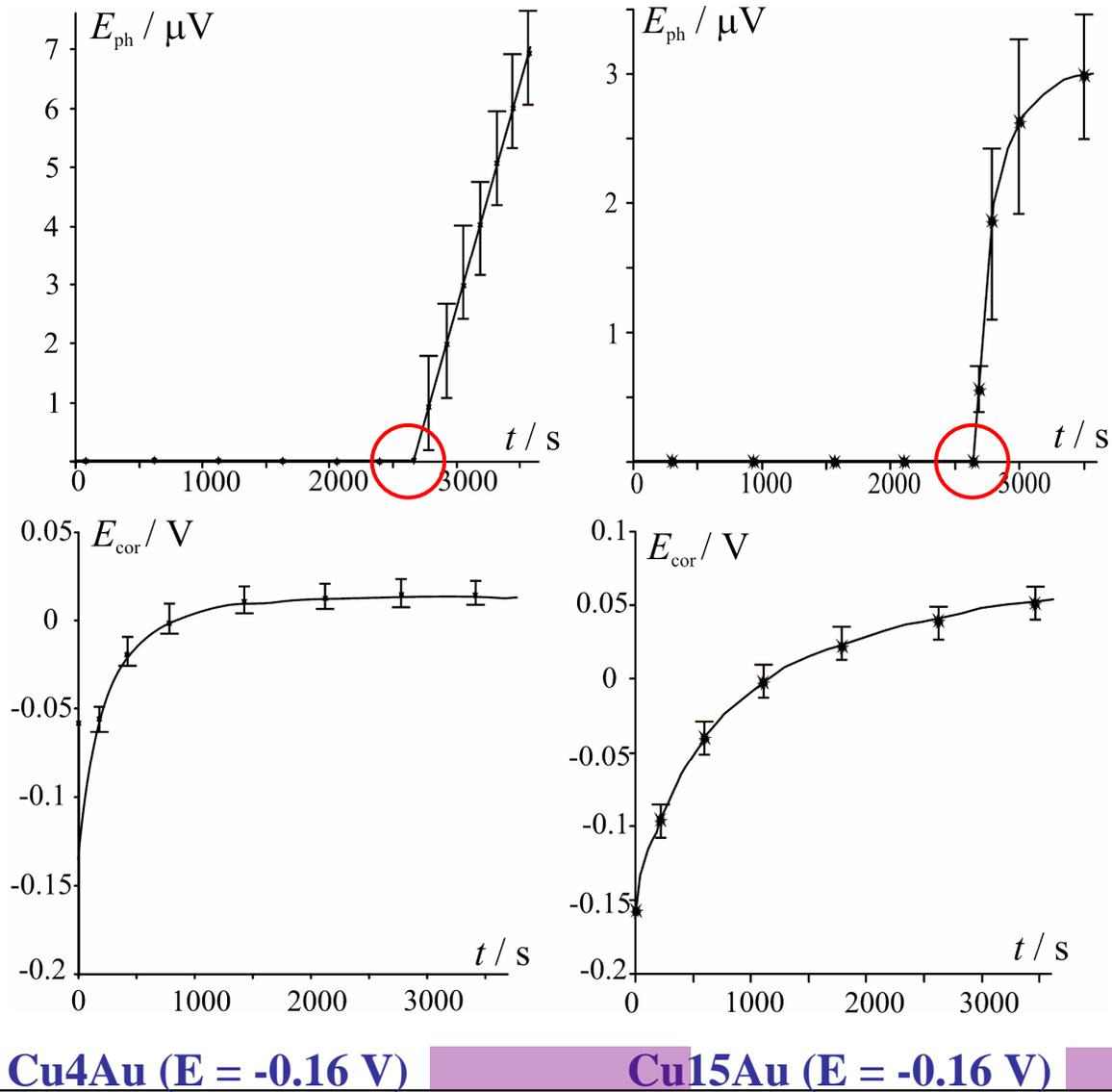
$$E_{ph} \sim L^2$$

$$L \sim t^{1/2}$$

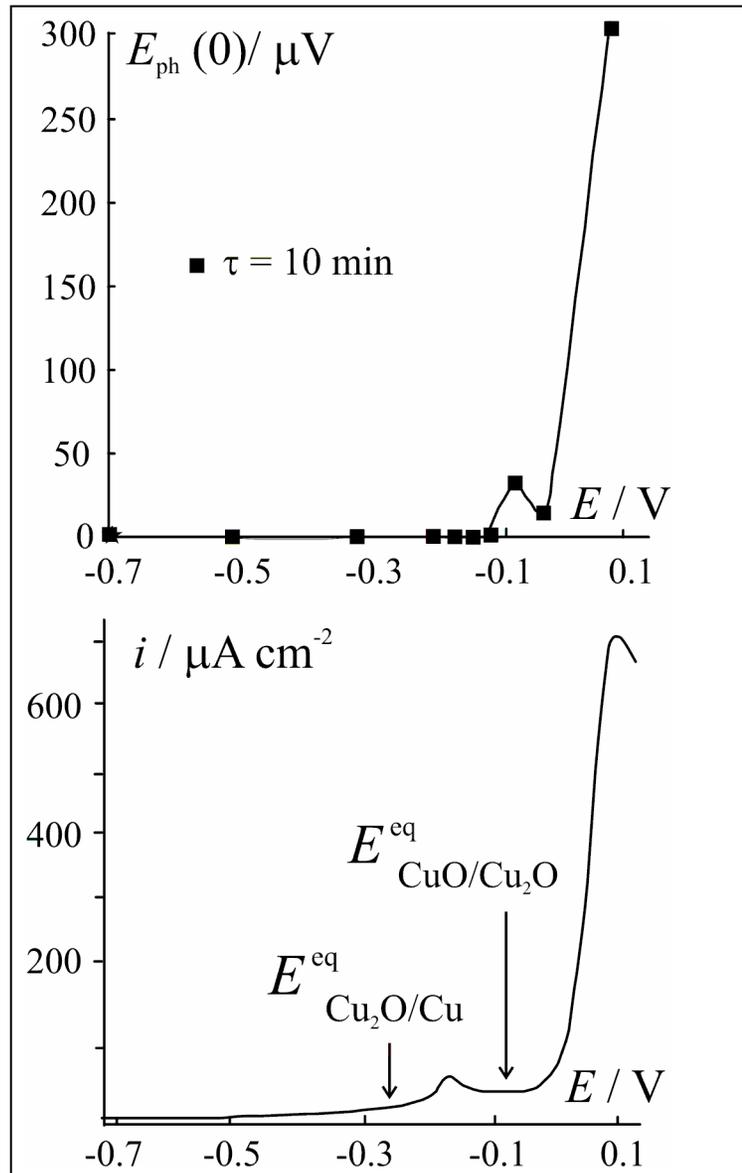
$$E_{ph} \sim t$$

The photopotential on copper surface in deoxygenated 0.1M KOH;  
 $\lambda = 400$  nm,  $\Phi_0 = 7.12 \cdot 10^{15}$  photon/cm<sup>2</sup> s

# Photopotential measurements on Cu and Cu-Au after the polarization in the range II ( $\lambda = 400$ nm)



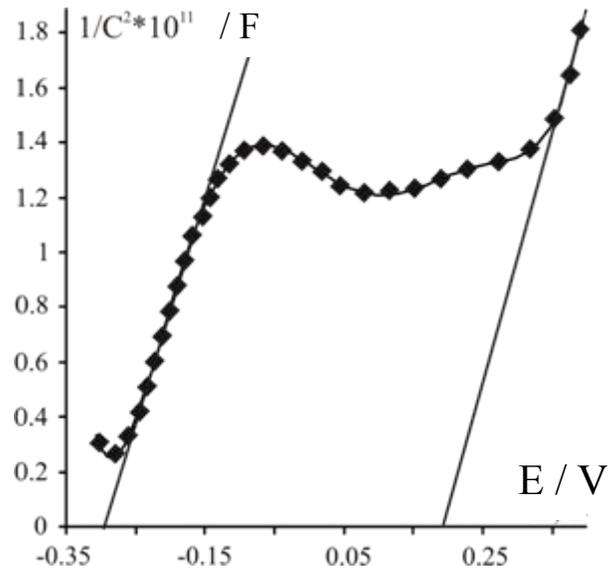
# The dependence of the initial photopotential (a) and polarization current (b) on the potential of Cu-electrode



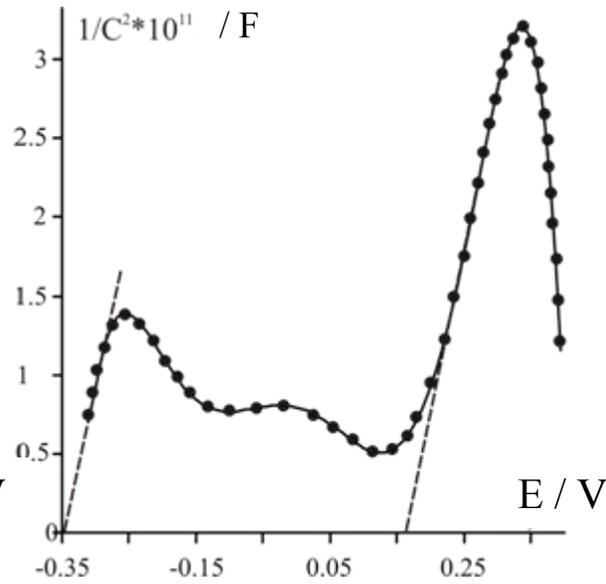
The clear-cut correlation between the  $E_{ph}(0) - t$  dependence and the voltammogram shows a close interrelation between the kinetics of the oxide formation and the oxide structure predetermining the value of the photopotential.

# Flat-band potential of $\text{Cu}_2\text{O}$ and $\text{CuO}$

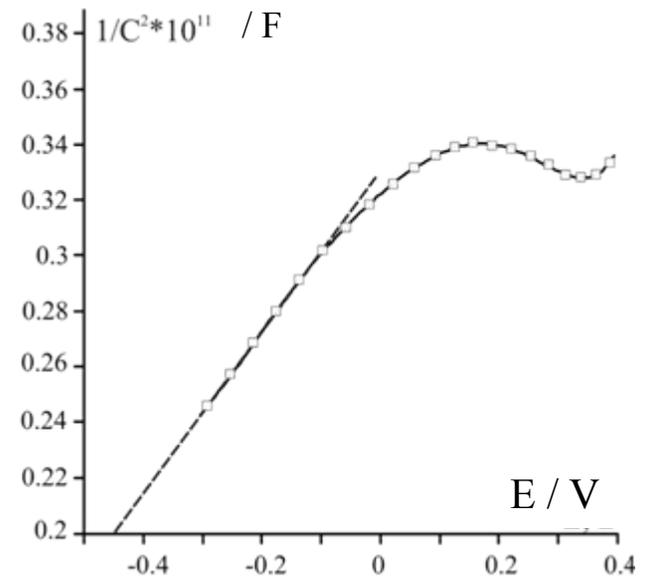
## Cu



## Cu4Au

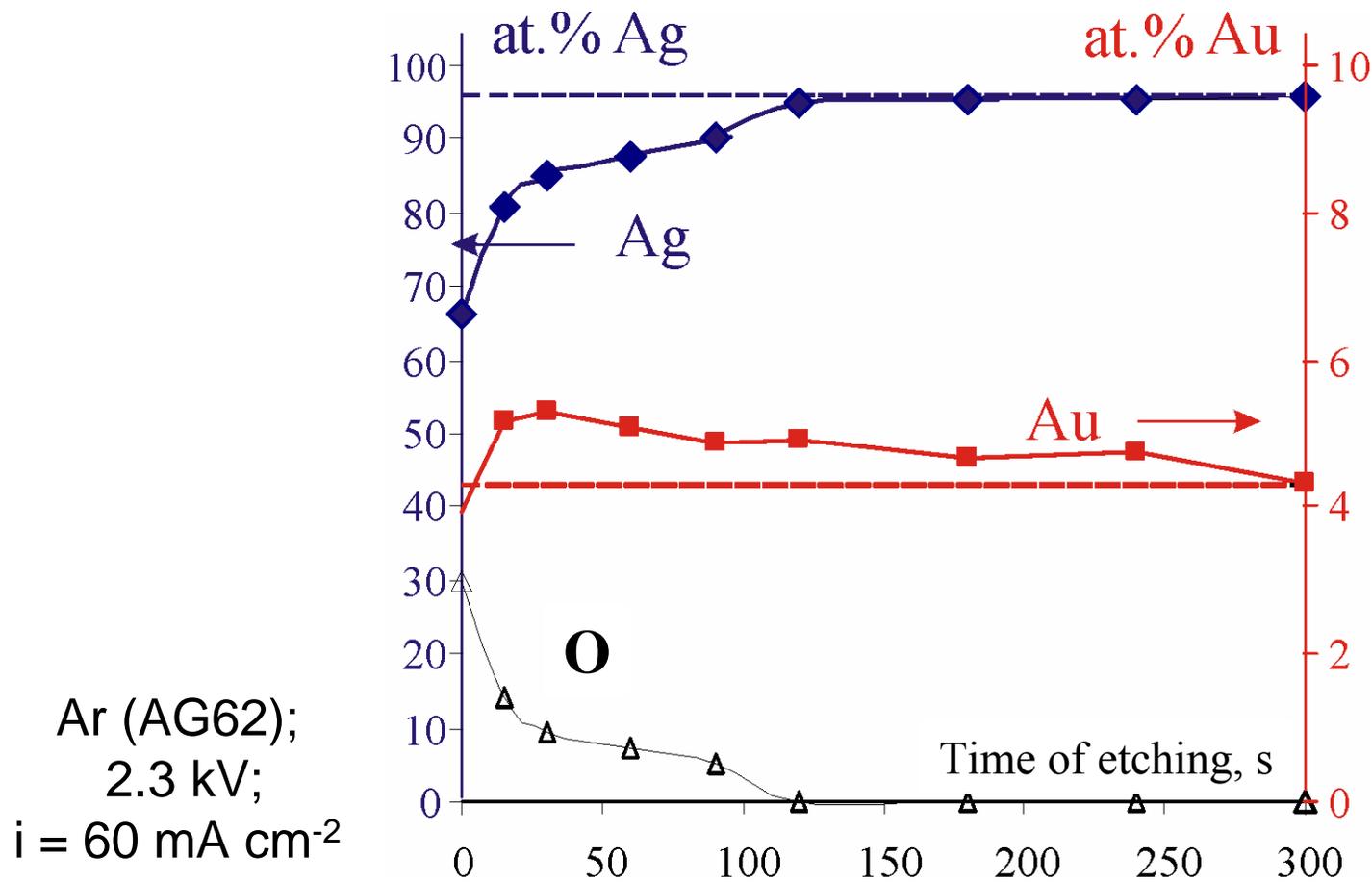


## Cu15Au



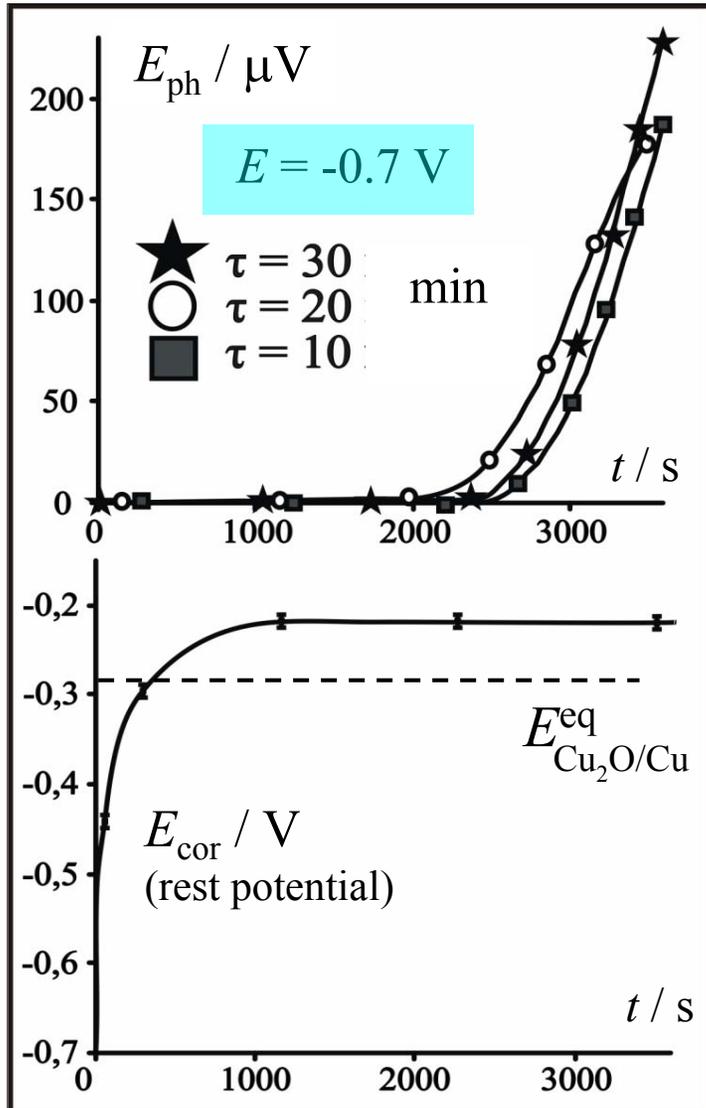
	Cu	Cu4Au	Cu15Au
$E_{\text{fb}}(\text{Cu}_2\text{O}) / \text{V}$	-0.30	-0.35	-0.45
$E_{\text{fb}}(\text{CuO}) / \text{V}$	0.20	0.15	-

# XPS-study of Ag<sub>4</sub>Au after Ag<sub>2</sub>O formation in 0.1 M KOH



We are grateful to professor Leonid Kazanskiy for help in this measurements

# Photopotential measurements on Cu and Cu-Au after the polarization in the ranges I and II ( $\lambda = 400$ nm)



$$L \sim t^{1/2}$$

$$E_{ph} \sim L^2$$

$$E_{ph} \sim t$$

