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Ellipsometry examination of copper alloys with transitive metals

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Abstract. Electron structure of copper alloys with 3d transition metals (Fe, Co and Cr) have been studied basing on ellipsometrical measurement of Δ and Ψ in wide spectral range $h\nu = 1.0\text{--}4.95$ eV. Spectral dependences of Cu-Cr alloys optical conductivity in wide range of chrome concentration ($C = 2.5\text{--}30$ at. %) have been minutely analyzed in this work. Ascertainment that in spectrums of studied alloys (and for copper alloys with other transitive metals) were observed basic band of pure Cu, in addition supplementary band in range 1-2 eV were observed too. Is shown that at small Cr concentrations ($C < 5$ at. %) alloy is forming a single band similar to copper, with insignificant dependence of Fermi level E_F from impurity concentrations. Besides there was founded that in electron structure appear impurity bands situated between Fermi level and d -band of copper. They split on 0.4 eV as a result of spin-orbit interaction. At high impurity concentrations ($C_{Cr} > 5$ at. %) the alloys are heterogeneous mixtures of pure transitive metals and copper based solid solution.

Keywords: Spectroellipsometry, refractive index, absorption index, optical conductivity, copper, alloy, transitive metals, energy structure, density of electron states, impurity bands.

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1. Introduction

Among all 3d transition metals, only Ni is well soluble in copper under formation of continuous series of solid solutions with fcc lattice [1]. Other transition metals, e.g., Fe, are low soluble, while Co and Cr, according to literature, are almost copper-insoluble [1]. In this case, optical characteristics, such as refraction n and absorption κ indices, the dielectric permeability ϵ and optical conductivity σ must be described by linear functions of impurity concentration. This is due to that, according to [1, 2], the alloys are heterogeneous mixtures of almost pure copper and impurity, thus, the experimental spectra of the mentioned quantities must be formed by superposition of spectra of the mentioned components with the corresponding weight coefficients.

In this work, the optical properties of binary copper alloys with low content of Fe, Co and Cr have been studied within the spectral range where the interband electron transitions play the main part. The results obtained evidence that the limiting solubility of Fe, Co and Cr in copper is substantially higher than it was believed before.

In the case of Cu-Ni solid solutions, a narrow d -band in electron spectrum has been revealed which is associated with Ni and is situated between the top of d -band and the Fermi level [2, 3]. Since other transition metals, espe-

cially Co, are closely similar to Ni in their physical properties, the formation of the impurity band in alloys is to be expected if those are single-phase. Before, a comprehensive research of impurity bands by optical method was carried out for a series of 3d transition metal alloys. In parallel, the electronic structure of disordered alloys was studied rather intensely using theoretic methods promoted by optical researches of the precious metal alloys [4, 5].

Studying the absorption spectra of Cu-Fe and Cu-Cr, it was determined that small impurities of Fe, Cr and Ni do not influence essentially the position of sp - and d -bands connected genetically with Cu. Changes in electron spectra of all the alloys, like the Cu-Ni ones, occur mainly between the top of Cu d -bands and the Fermi level E_F due to formation of the impurity band (with position depending on impurity type), in spite of different solubility of the mentioned metals in copper. Optical methods allow getting a series of parameters characterizing the impurity band, for example, its half-width Δ , its center position with respect to the Fermi level $E_d - E_F$, and a series of other electron parameters can be calculated proceeding from the above ones.

2. Experimental details

The optical properties of Cu-Fe, Cu-Co and Cu-Cr alloys have been studied basing on the constants n and κ meas-

ured at ambient temperature within the wavelength range $\lambda = 0.25\text{--}1.24 \mu\text{m}$ (or photon energy range $h\nu = 1.0\text{--}4.95 \text{ eV}$) by ellipsometric method. The samples of alloys with impurity content from 2.5 to 40 at. % are prepared by vacuum arc melting in argon atmosphere using several consecutive melting's. The samples were annealed for 24 hours in the same atmosphere at 900°C to provide the most possible homogeneity. The mirror surfaces of samples were prepared by mechanical grinding and polishing by diamond powders and pastes of different abrasive grain sizes. The recrystallisations anneal in vacuum at 450°C during 3 hours and electric polishing was carried out to remove surface strains.

3. Experimental results and discussion

The curves of the optical conductivity dispersion $\sigma(h\nu)$ are of the most interest in studying optical properties of the alloys. Using these curves, the data can be obtained on the changes in electron spectrum of copper doped with 3d transition metals, because σ is connected directly with interband density of electron states [6]. The experimental curves $\sigma(h\nu)$ for Cu-Fe, Cu-Co and Cu-Cr alloys are shown in Figs 1–3, respectively. In these Figures, the curves for pure components are presented, too.

It is seen that within the photon energy region $h\nu < 1.5 \text{ eV}$ the optical conductivity σ of copper monotonously increases as $h\nu$ decreases. This means that it is just free electrons that contribute mainly to absorption due to transitions within each band crossing the Fermi level. In Cu-Co alloys, as well as in Cu-Cr ones, the contribution of free carriers are almost unobservable within spectral range under study. From our own data that the characteristic peculiarities of the copper optical spectrum are sharp edge of the interband absorption at the photon energy $h\nu = 2.1\text{--}2.3 \text{ eV}$ as well as very intense absorption band with a maximum at photon energy about 4.62 eV . These peculiarities of the copper optical spectrum are

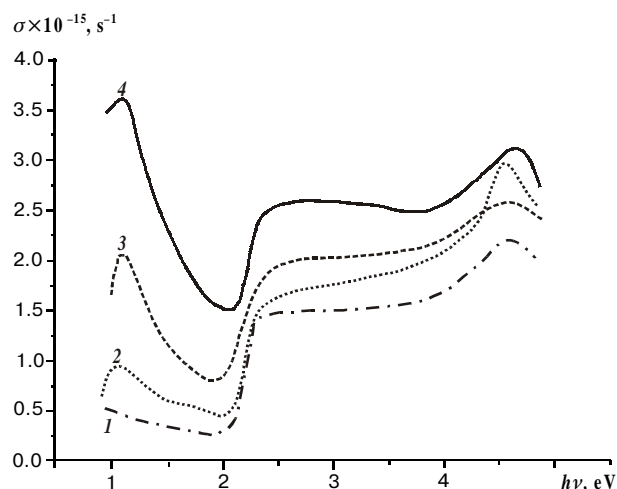


Fig. 1. Optical conductivity of pure Cu (1) and for Cu-Fe alloys with Fe content (at. %): 7.5 (2), 15 (3) and 30 (4).

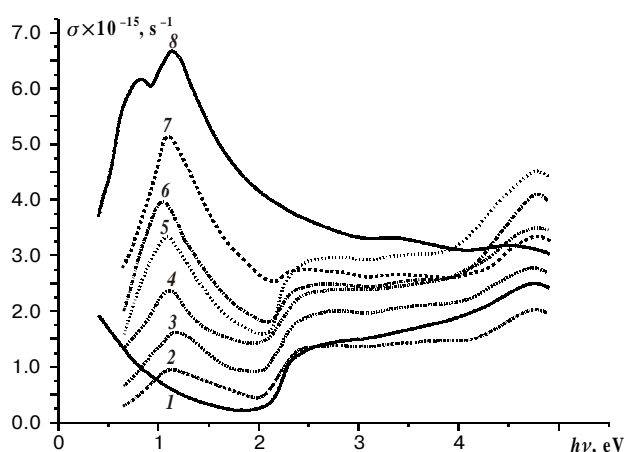


Fig. 2. Optical conductivity dispersion of Cu-Co alloys with Co content (at. %): 2.5 (2), 5 (3), 10 (4), 17.5 (5), 30 (6) and 50 (7) as well as for pure Cu (1) and Co (8). Curves 3 and 7 are lifted up by $5 \cdot 10^3 \text{ s}^{-1}$ and 4–6, by 10^4 s^{-1} .

manifested, to a higher or lower extent, for all alloy samples. The experimental data allow evaluating the threshold of the optical interband absorption as the half-sum of the energy values corresponding to maximum and minimum σ near the absorption edge. This value is equal to 2.2 eV for pure copper but in alloys it is within limits of $2.21\text{--}2.24 \text{ eV}$, i.e. remains essentially unchanged upon Co and Cr addition to the alloy. In all alloys studied, there is also the main band with a maximum at $4.58\text{--}4.65 \text{ eV}$, i.e. the band is shifted along the energy scale by $0.3\text{--}0.4 \text{ eV}$ only with respect to the maximum for copper. Except for these two features, a weak maximum is revealed for alloys at photon energy $3.5\text{--}3.6 \text{ eV}$ that is more pronounced for alloys with high Cr content. We cannot find experimentally that maximum for the pure copper although it is very pronounced in the theoretical $\sigma(h\nu)$ curve constructed using the calculated electron spectrum data for this metal.

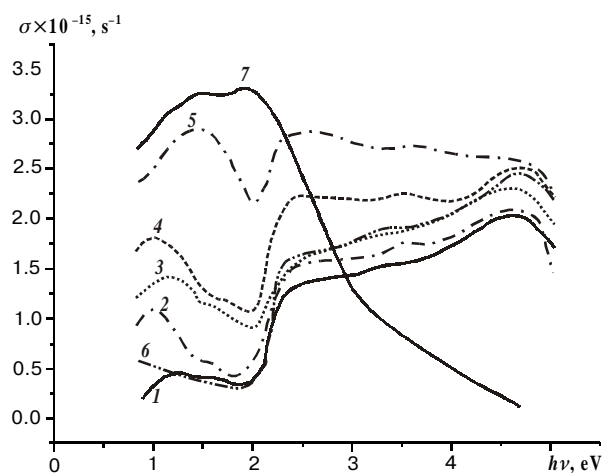


Fig. 3. Optical conductivity of Cu-Cr alloys with Co content (at. %): 2.5 (1), 5 (2), 10 (3), 17.5 (4) and 30 (5) as well as for pure Cu (6) and Cr (7). Curve 4 is lifted up by $0.3 \cdot 10^3 \text{ s}^{-1}$ and 7 by $3.6 \cdot 10^4 \text{ s}^{-1}$.

Alloying of Cu with Co and Cu with Cr is found to cause a strong effect, namely, appearance of a very intense band in $\sigma(h\nu)$ curves in the near IR region of the absorption spectrum at the photon energy $h\nu$ from 0.8 to 1.8 eV. Its intensity increases monotonously with increasing impurity content. For Cu-Cr alloys, this band has composite structure and consists of a several components. For the alloys containing 2.5 at. % Cr, these maximums correspond to the photon energy 1.34 and 1.70 eV (Fig. 3). At Cr concentration 5 at. %, the long-wave band intensity increases sharply but its maximum becomes shifted towards lower energy values by about 0.26 eV. At a further increasing of Cr concentration, the long-wave band intensity increases but not so sharply. The maximum of this band for alloys with Cr content 10 and 17.5 at. % is at photon energy 1.10 and 1.24 eV, respectively. In the alloy with 30% Cr, only one absorption band with a maximum at 1.50 eV is observed. It should be noted that there are no peculiarities in the energy range 1.10–1.34 eV where the maximum of the long-wave band is situated in $\sigma(h\nu)$ spectra of pure Cu, Co, and Cr. For copper, a slight increase in σ as the photon energy decreases is characteristic in the mentioned range, which is connected with free carrier absorption. In addition, the fact is worth to note that for the alloys, the intensity of high-energy maximum at 4.65–4.75 eV associated with Cu depends very weakly on the impurity concentration. The mentioned facts evidence that the $\sigma(h\nu)$ spectra of the alloys cannot be obtained by simple superposition of Cu and Cr as well as of Cu and Cr ones with corresponding weight coefficients, as could be expected according the data of the well-known reference book [1] where the solubility of Co and Cr in copper is said to be not more than 0.8 at. %.

In other words, in accordance with [1], e.g., Cu–Cr alloys comprise two phases: almost pure Cr and Cu–Cr solid solution (the concentration $N_{Cr} < 0.04\text{--}0.8$ at. %). The results of the computer simulation have shown that the optical conductivity spectra of alloys cannot be obtained by simple summation of those for pure Cu and Cr with weight coefficients determined by the lever rule [1]. Moreover, the experimental spectra cannot be get also under suggestion that the alloy components are pure Cr and solid solution Cu–Cr at Cr concentration of 2 at. %. The experimental spectrum agrees well with the calculated one in the case when Cr solubility in Cu is suggested to be not less than 5 at. % and increases further as the Cr concentration rises. Almost the same situation takes place in Cu–Co alloys.

Here after, let Cu–Cr alloys be considered in more detail. Taking into account the results of electron structure research of pure copper and its optical spectrum, a model of electron structure for the Cu–Cr solid solution can be proposed basing on the data obtained. In accordance with [7], the absorption edge for pure copper at photon energy 2.1–2.2 eV is associated with the electron transition from the top of d-bands near the L_3 point of the Brillouin band to unoccupied states of L_2' type sp -bands in the vicinity of the Fermi level E_F . The energy band structure of copper is shown in Fig. 4 where the possible

transitions forming the optical conductivity spectrum $\sigma(h\nu)$ are shown by the arrows. From the experimental data on the optical properties of Cu–Cr alloys and the interpretation of the absorption edge, a conclusion can be drawn that for the Cu–Cr solid solution, not only the distance between the d -band top and the Fermi level remains unchanged but the whole structure of bands shifted from Fermi level by 2.2–2.3 eV does not change.

The intense absorption above the absorption edge is connected with electron transitions in a large volume of the Brillouin band [8] in directions L – W and X – F (the possible transition are shown on Fig.4 by arrows). The optical spectrum ($h\nu$) in the photon energy range 2.5–4.0 eV results from the superposition of different bands associated with these transitions. Since the $\sigma(h\nu)$ spectrum character of Cu–Cr solid solutions remains almost unchanged in the mentioned range, the structure of bands shifted from the Fermi level by 2.5–4.0 eV in photon energy remains the same as for the pure Cu. At last, the absorption spectrum character in the photon energy range 4.0–5.0 eV where the main absorption band of pure copper connected with transitions from L_3 d -states to free levels of L_1' (see Fig. 4) does not change essentially in the alloys. Thus, the structure of s, p, d -bands shifted up to 5 eV from the Fermi level is the same as in pure copper.

Thus, the study of optical properties of Cu–Cr alloys with low Cr content (where it is well soluble in Cu) show that the s, p, d -bands of copper remote at least 5 eV from the Fermi level remain unchanged in their structure and energy spectral position. An impurity band is formed due to Cr situated under the Fermi level. Supposing that the new absorption band in the $\sigma(h\nu)$ optical spectra of Cu–Cr alloys in the photon energy range 0.8–1.6 eV is related to electron transitions from the impurity d -underband to free electron states near the Fermi level, the position of impurity band center with respect to the Fermi level, $E_d - E_F$, and its half-width can be found basing on the experimental data.

The above facts indicate that Cu d -bands can be smoothed out without any essential shift along the energy scale due to Cu and Cr d -states hybridizing occurring when Cr concentration in the alloy increases. Moreover, an impurity band is formed situated under Fermi

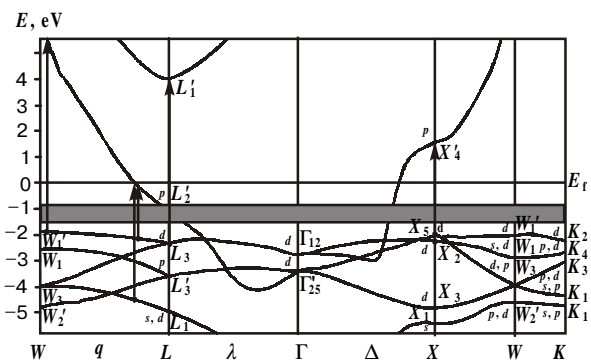


Fig. 4. Energy bands for Cu–Cr alloys. Region of possible dipole transitions of electron shown by arrows. The impurity band of Cu and Cr solution is shadowed.

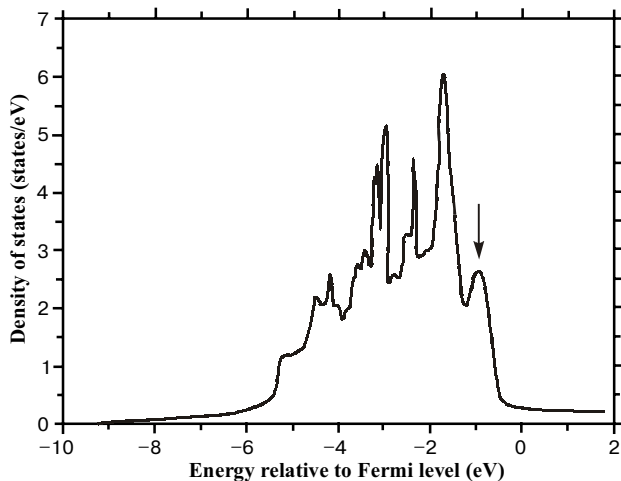


Fig. 5. Calculated state densities $N(E)$ for Cu-Cr alloy with Cr content 5 at. %. The portion formed by impurity states, pointed by arrow.

level E_F with $E(h\nu)$ increasing slightly with Cr concentration in the solution. If Cr would be well soluble in Cu, a single band of the alloy should arise at high Cr concentration in the alloy, similar to the case of Cu-Ni [3, 9]. However, according to our data, the maximum Cr solubility in Cu is not high (although being substantially higher than it was believed before) and it exceeds slightly 5 at. %.

The state density $N(E)$ within the impurity band can be calculated basing on experimental data [8], processing from models of that band. On Fig. 5, the state density curves for the impurity band of Cu-Cr solid solutions with 5 at. % Cr is presented. Roughly speaking, the state density $N(E)$ for each mentioned solid solution is equal to the sum of state density within limits of the impurity band and that for pure copper.

4. Conclusions

It follows from the studies that the energy bands of alloys are similar to Cu at low Cr concentration when it is soluble well in Cu and Cr forms the impurity band situated nearly in the middle between the Cu d -band top and the Fermi level E_F . Another variant is also possible which explains the nature of the low-intensity absorption band of the alloys in the range 1.6–1.7 eV. If it is assumed that incomplete solubility takes place even at small Cr amounts in copper, so that Cr clusters are formed, then the absorption band similar to Cr one is formed due the absorption by the clusters. The second Cr absorption peak at 1.95 eV in the spectra may not appear because it is in the range of absorption minimum of pure copper. With increasing Cr concentration, it is possible that the size of clusters and their number increase only insignificantly, because Cr solubility in copper is increased. As Cr content increases, the structure of Cu d -bands becomes slightly smoothed out without any essential shift along the energy scale. With increasing Cr concentration, the impurity band is

widened and at high Cr concentrations, a single band of alloy can be formed at last. This cannot be realized to the full measure in the alloys under study, because the Cr solubility in Cu is limited, as is shown by the results of optical properties study on the alloy containing 30 at. % Cr. It follows from the data presented that the electron spectrum of Cu-Cr alloys is rather complicated. At low Cr concentrations (where it is well soluble in Cu), the energy bands of the alloys are similar to those of copper while the Cr impurity forms an additional band situated between the top of Cu d -band and Fermi level. The appearing of the impurity band in Cu-Cr alloys is indisputable and it results in change of other physical properties of the alloys. At high Cr concentrations, clusters of this metal are formed, and the experimental spectra of the alloys are resulted from the superposition of spectrum of Cu-Cr solution containing not less 5 at. % Cr and that of pure Cr.

The determination of the limiting Cr solubility in Cu is the most important result of Cu-Cr alloy optical properties study; it exceeds slightly 5 at. %. The optical method turned out to be extremely sensitive in determining the limiting Cr solubility in Cu as well as that of Co and Fe [10].

By studying the optical properties, it is found that at impurity concentrations $C < 10$ at. %, optical characteristics, such as refraction and absorption indices, dielectric constant, optical conductivity and the reflection coefficient under the normal incidence $R = ((n-1)^2 + \kappa^2) / (n+1)^2 + \kappa^2$, depend non-linearly on the impurity concentration. This is due to a complicated transformation of the copper electron spectrum in the presence of Fe, Co, or Cr additives. At high impurity concentrations ($C > 10$ at. %), the alloys contain two phases and are heterogeneous mixtures of the almost pure Fe, Co or Cr and a copper-based solid solution containing about 95% Cu. Experimental dependences of the mentioned optical characteristics on the wavelength result from superposition of Fe, Co or Cr spectra and that of the mentioned solid solution with according weight coefficients

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