

OPTICAL SPECTROSCOPY OF CuAl ALLOYS UNDER ION BEAM SPUTTERING

M. Ait El Fqih^{1,2,*}, A. Kaddouri¹

¹ *Equipe de Spectroscopie & Imagerie Atomiques des Matériaux, Université Cadi Ayyad, Marrakech – MAROC*

² *Faculté Polydisciplinaire, Université Chouaib Doukkali, El Jadida – MAROC*

**E-mail: m.aitelfqih@gmail.com*

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Abstract–Light emission during 5 keV Kr⁺ ion bombardment of CuAl alloys with different concentration is studied. The transient effect phenomenon has been investigated under two pressure conditions: one at base pressure ($\sim 10^{-7}$ torr) and the other with introduction of oxygen gas ($\sim 10^{-4}$ torr). The experimental oxygen sputtering yield was combined with simulation using the SRIM-code program. Both of them were in fairly good agreement.

Keywords: photon emission, transient effect, simulation, CuAl alloys

1. Introduction

During fast keV ion-bombardment of solid targets, many secondary processes occur such as reflection of projectiles, electron ejection, sputtering of atomic and molecular species [1, 2]. Also light emission is observed and can provide some information about the mechanism of excitation and de-excitation in front of bombarded surfaces [3, 4]. Furthermore excitation in sputtering with oxygen atmosphere is much more complicated and even less understood in case of alloy targets [5]. Explanations of the excited state populations in terms of direct excitation in atom-atom collisions in the cascade, atom-surface electron transfer, bond breaking and the local thermal equilibrium processes have been proposed so far [6]. Agarwal et al. [7] observed that the photon intensity depends strongly on the surface condition during bombardment of CuBe alloy by 6 keV O₂⁺, this phenomenon was interpreted by a model of overlapping of individual collision cascades. Dogar et al. [4] assumed that the dominating effect in the production of excited atoms and ions in the case of ion beam sputtering of YBaCu₃O₇ by 1–10 Ar⁺ ions is the electron exchange mechanism between sputtered particle and surface.

One of the most primary effects in ion-solid interaction is known as the transient effect which means the change of line intensity as a function of time of bombardment. This behavior was initially reported by van der Weg et al. [8] and Kelly et al. [9]. They suggested that this phenomenon is due to the change of adsorbed oxygen exposure on the surface. They eventually developed a model for quantitative analysis of transient effect phenomenon. Recently [10, 11], the transient effect issue was thoroughly experimented generally since there is a close parallel to the experiments made on the secondary ion emission [12].

The purpose of the following work is to better understand the ion-induced secondary photon emission processes when the target is exposed to a variation of oxygen pressure. It reports the

experimental results of the light emission from sputtered Cu and Al atoms from three alloys with different concentration ($\text{Cu}_{90.6}\text{Al}_{9.4}$, $\text{Cu}_{28.6}\text{Al}_{71.4}$ and $\text{Cu}_{21.6}\text{Al}_{78.4}$).

2. Experimental

The experimental setup, employed in the following work, concerning ionic bombardment of solid surfaces has been portrayed in great detail elsewhere [13, 14]. Briefly, Kr^+ ions are formed by electron impact on Kr (99.998% purity) in a plasma source. Ion currents of a few microamperes of 5 keV Kr^+ beam was transmitted on the target mounted inside an ultra-high vacuum chamber, where the residual pressure was lower than 10^{-7} torr. When alloys surface was used, pure oxygen (air liquid 99.995% grade purity) was presented at a pressure of 5×10^{-6} torr in the presence of the target. The gas pressure was measured by a Penning gauge (CF 2P). Before actual experiment, targets were cleaned in-situ by ion beam sputtering. The ion beam current was measured by a Faraday cup placed behind the target along the ion beam direction. Typical beam current densities in these experiments were around $1 \mu\text{A}/\text{mm}^2$. The ion beams were incident at an angle of 70° with respect to the normal of the surface. The light emission was analyzed via a HR 320 Jobin Yvon monochromator, equipped with an 1800 groves/mm holographic grating and transmitted onto a Hamamatsu R4220P photomultiplier which is sensitive to the wavelengths located between 190.0 and 650.0 nm. A micro-computer controls the whole detection system through the Prism program. CuAl alloys were produced by induction melting and solidification in situ. Three alloys were studied, $\text{Cu}_{90.6}\text{Al}_{9.4}$, very close to the single phase Cu₄Al of mass composition $\text{Cu}_{90.4}\text{Al}_{9.6}$ and the hypoeutectics $\text{Cu}_{28.6}\text{Al}_{71.4}$ and $\text{Cu}_{21.6}\text{Al}_{78.4}$. A hypoeutectic is made of pure Al zones interdigitated with eutectic zones with a typical spacing of 10-100 μm .

The simulation was done with the well-tested SRIM-code for a large number of incident ions and let the computer count the number of copper and aluminium atoms emitted in the solid angle corresponding to each probe [15]. In this program it is assumed that the collisions between atoms can be approximated by elastic binary collisions described by an interaction potential. It is further assumed that the energy loss to electrons can be handled separately as an inelastic energy loss. SRIM-code requires several ingredients. Some of them (energy and incidence angle of the ions) are experimental. The other ones are three phenomenological energy parameters, namely $E_d = 25$ eV, the displacement energy, $E_b = 3$, lattice binding energy, and E_s the surface binding energy (3.52 eV for Cu and 3.36 eV for Al).

3. Results and discussion

The optical spectra are measured with a resolution of 0.32 nm. They show the presence of several fine lines. Transient of photon emission of Cu I 324.8 nm and Al I 309.3 nm lines obtained

from 5 keV Kr^+ ion bombardment on $\text{Cu}_{90.6}\text{Al}_{9.4}$, $\text{Cu}_{28.6}\text{Al}_{71.4}$ and $\text{Cu}_{21.6}\text{Al}_{78.4}$ alloys target are given in Fig. 1(a-c) and Fig. 2(a-c). These two lines were chosen in view of the fact that they were relatively more intense. The transient effect has been studied under two conditions: one at base pressure ($\sim 10^{-7}$ torr) and the other with the introduction of oxygen gas ($\sim 10^{-4}$ torr). For both Cu and Al, the decay mode is essentially exponential. The characteristic decay time is much longer for Al than that for Cu (see Table 1). Similarly, the same phenomena were observed by Agarwal et al. [7] during bombardment of CuBe alloy under 6 keV O_2^+ and interpreted by the process of the oxygen incorporation at the constituent of the alloy which are quite different. The decay of spectral line intensity for Al and Cu is found to be analogous to that of the results presented for Al by Kelly et al. [9] and for Ni and Fe by Agarwal et al. [5]. According to these others, the observed curve may be attributed to the change of surface oxygen coverage formed to adsorbed and recoil-implanted oxygen atoms at Al and Cu sites. In view of the fact that the oxide bond energy per metal atom for Al (10.26 eV [16]) is far greater than that of Cu (1.79 eV [17]) preferential oxidation of Al is most likely.

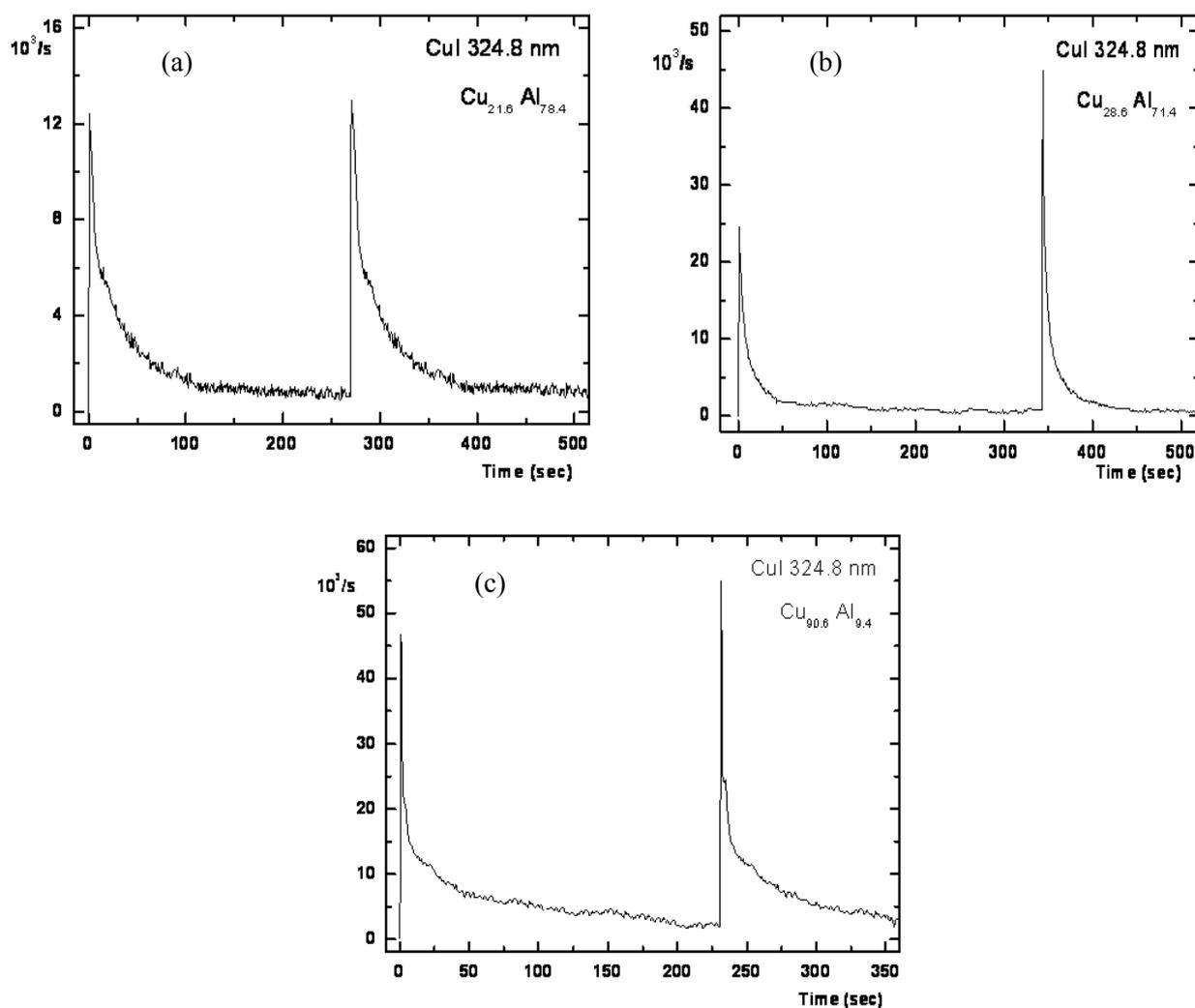


Fig. 1. Transient of Cu I 324.8 nm line during Kr^+ bombardment of (a) $\text{Cu}_{21.6}\text{Al}_{78.4}$, (b) $\text{Cu}_{28.6}\text{Al}_{71.4}$ and (c) $\text{Cu}_{90.6}\text{Al}_{9.4}$.

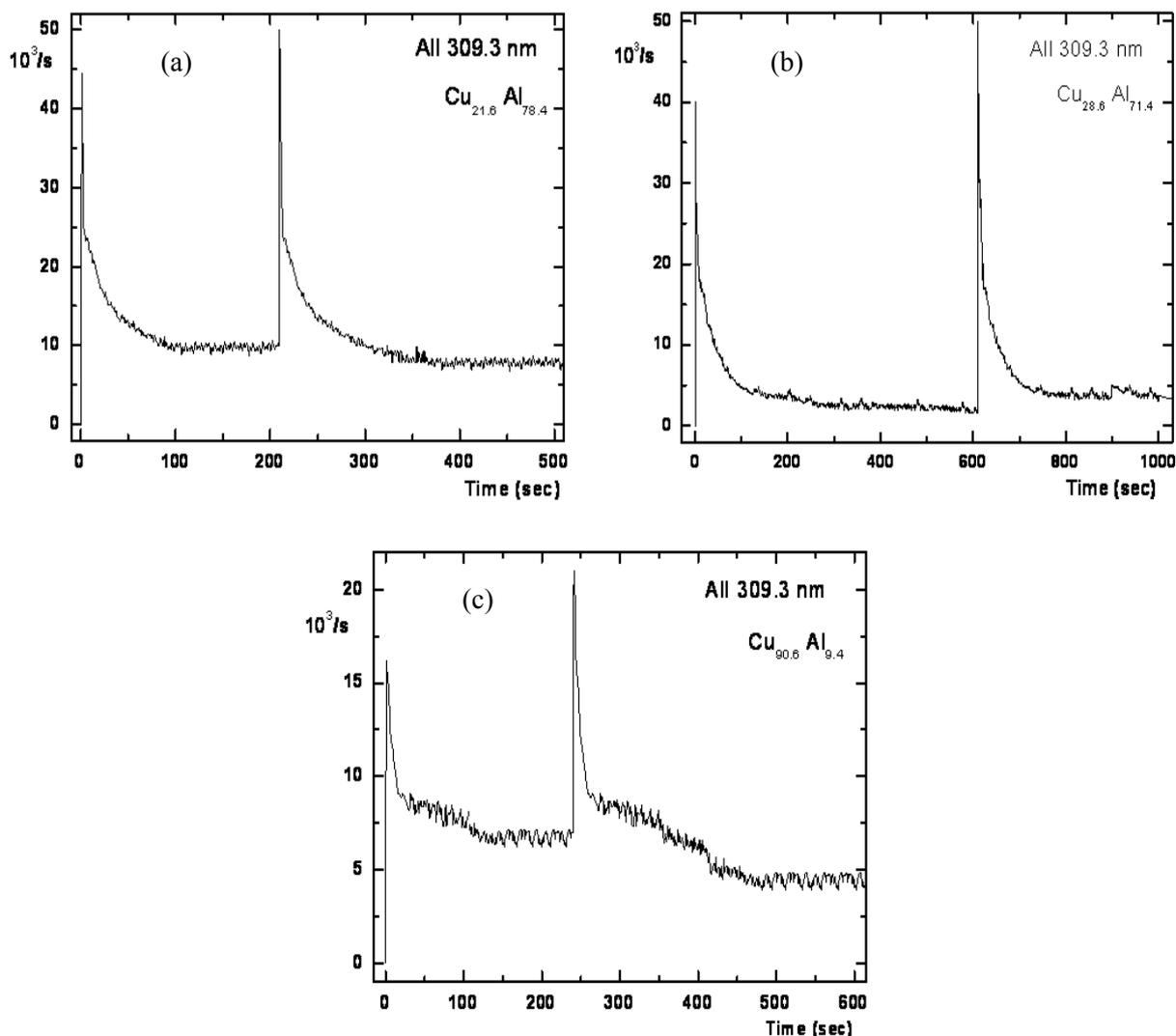


Fig. 2. Transient of Al I 309.3 nm line during Kr^+ bombardment of (a) $\text{Cu}_{21.6}\text{Al}_{78.4}$, (b) $\text{Cu}_{28.6}\text{Al}_{71.4}$ and (c) $\text{Cu}_{90.6}\text{Al}_{9.4}$.

In order to better understanding how sputtering rates of adsorbed oxygen depends on the concentration of copper and aluminium in CuAl alloys, oxygen sputtering yield Y_O for Al and Cu for each studied alloy is calculated (see Table 2) using the formula

$$Y_O = \left(\frac{0.693n_s}{t_{1/2}\Phi_i} \right) \quad (\text{Eq. (6) in [18]}).$$

Here n_s is the surface atom density with a value in the present case 1.06×10^{15} atoms/cm², the half-time ($t_{1/2}$) values are obtained from the full width at half maximum (FWHM) of photon intensity profiles in Fig. 1 (a, b and c) and Fig. 2 (a, b and c), Φ_i is the ion flux density. The SRIM-code program is used to calculate theoretically the oxygen sputtering yield. Surface binding energy is taken as 3.52 eV for all investigated alloys. Only the first oxygenated monolayer is considered. Table 2 shows a good agreement between theoretical and experimental values of oxygen sputtering yield.

Table 1. Decay time of Cu and Al in CuAl alloys.

Alloy	Decay time of Al (s)	Decay time of Cu (s)
Cu _{90.6} Al _{9.4}	480	90
Cu _{28.6} Al _{71.4}	250	110
Cu _{21.6} Al _{78.4}	170	120

Table 2. Sputtering yield values (Y_o) of adsorbed oxygen on Cu and Al in CuAl alloys.

Alloy		Beam current (μ A)	Ion flux density, Φ_i (ions/cm ² /s)	$t_{1/2}$ values (Figs. 1 and 2) (sec)	Y_o values (atoms/ion)	
					present results (Eq.(1))	SRIM-code results (simulation)
Cu _{90.6} Al _{9.4}	Al	1.7	2.12×10^{13}	49.00	0.70	0.89
	Cu			2.50	13.86	13.20
Cu _{28.6} Al _{71.4}	Al	1.3	1.62×10^{13}	5.70	7.96	8.89
	Cu			7.64	5.94	5.33
Cu _{21.6} Al _{78.4}	Al	1.5	1.87×10^{13}	4.50	8.73	8.96
	Cu			9.83	4.00	3.80

4. Conclusions

Transient effect was investigated for Cu I 324.8 nm and Al I 309.3 nm. The decay mode was essentially exponential for Cu and Al. The preferential oxidation of Al was most likely. The experimental oxygen sputtering yield was compared with simulation and was in fairly good agreement.

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