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Experimental and numerical study of surface alloying by femtosecond laser radiation

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ABSTRACT

Here we report on experimental studies of femtosecond laser induced surface metal alloying. We demonstrate that layers of different metals can be mixed in a certain range of laser pulse energies. Numeric simulations demonstrate that the sub-surface melting and mixing is advantaged through the difference in the electron–phonon coupling constants of the metals in the multi-layer system. Dependence of the depth of the mixed layer on the number of laser pulses per unit area is studied. Numeric simulations illustrate physical picture of the laser alloying process.

1. Introduction

Laser processing of metallic surfaces is known to change material properties, e.g. material hardening or alloying of heterogeneous samples can be achieved in this way [1]. This has been experimentally demonstrated for CW and nanosecond pulsed lasers [1–3]. Surface laser alloying techniques involve two main steps: Depositing of the alloy compounds on the substrate and illuminating the area with the laser radiation. The alloy components are deposited either layer-by-layer or simultaneously. Laser beam of sufficient fluence can melt and mix the components, which resolidify as alloy. Convective mixing was found to play the key role in the alloying processes [4] since it provides a more effective mixing mechanism than diffusion. The frozen bimetal structure may be analysed e.g. by means of common experimental techniques with nano-scale resolution such as X-ray photoelectron spectroscopy (XPS) [5] or scanning electron microscopy (SEM).

Application of femtosecond lasers is a promising extension of this technique since this may be a key for producing alloys of immiscible compounds due to very rapid melting and solidification processes. Femtosecond laser pulses are absorbed in a thin surface layer and trigger quick sample heating with a heating rate of approximately 10^{14} K/s [6]. A shallow layer of metal melt appears and mixing of the metals constituting the sample starts. After that a very rapid (with cooling rates of more than 10^{12} K/s [7]) resolidification occurs under such conditions. Such a quick cooling timescale allows to suppose that even immiscible melts will not segregate into two fractions and exotic alloys can be produced in this way.

On the other hand such a quick melting and solidification result in a very short time window for the metals to mix. Moreover, heat diffusion is slower than energy deposition into the electronic subsystem if a femtosecond laser is employed. Hence the deposited energy is confined in a thin surface layer defined mostly by the optical attenuation length of the laser radiation and the penetration depth of the hot electrons. This is advantageous for laser ablation, but reduces the depth of the melt layer and limits laser fluence at which alloying happens without simultaneous ablation of the alloy. This raises the question whether metal mixing and hence surface alloying is really possible by femtosecond laser processing.

Here we present experimental and numeric study of surface metal mixing on an example of Au/Cu bimetallic layers exposed to femtosecond laser pulses. Liquid Au and Cu are miscible but they are chosen to test whether the mixing is possible upon femtosecond laser surface heating. We demonstrate formation of an alloyed layer in a certain range of process parameters. The depth of the alloyed layer can be controlled by the spatial density of laser pulses. Physical picture of the laser alloying process is illustrated with numeric simulations.

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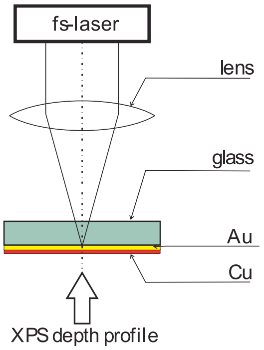

Fig. 1. Schematic representation of the experimental arrangement. Direction of sputtering for XPS analysis is shown by the arrow.

2. Experimental setup

Studied bimetallic structures consist of two metal layers subsequently deposited onto a plane glass substrate. Vacuum-evaporation techniques are used for deposition of the metal layers. The thickness of the layers is controlled by quartz crystal microbalance. The structure is exposed to femtosecond laser radiation of a Ti:sapphire laser (*Hurricane*, *Spectra Physics*) with pulse duration $t_p \approx 120$ fs, and wavelength of 800 nm. The laser pulse energy is adjusted by means of a Glan–Thomson prism and a $\lambda/2$-plate. The average pulse energy is controlled by laser power-meter *Coherent, Fieldmaster GS*. The laser fluence F on the surface can be estimated as the ratio of the measured energy and the crater area.

The laser beam is focused on the metallic surface through the glass substrate so that the topology of the outer metal surface surely stays unchanged in the course of the laser processing, see Fig. 1. Such an arrangement eases following measurements of the depth profiles by means of X-ray photoelectron spectroscopy. The intensity profile of the laser beam is not homogeneous but has a Gaussian radial profile. The inhomogeneous deposition of laser energy may result in inhomogeneities in the laser-induced alloying, which would complicate the interpretation of the XPS in-depth profiling. In order to decrease the effect of the beam profile, the sample is processed in a computer-controlled XY-stage *New wave, UP-XP*, which is programmed to run a raster pattern with a high overlap of single laser shots [8].

Indeed if raster pattern is applied for the laser-induced alloying, the effect of inhomogeneous Gaussian beam profile is reduced by overlapping of several shifted laser pulses as the laser spot runs along one line and by changing from one line to the next one. The number of laser shots interacting with a surface element can be estimated as: $N = \frac{d^2 f}{v\,\delta y}$ [8], where d is the diameter of the laser spot, f – the laser repetition rate, v – the linear velocity of the spot on the sample surface, δy – the interline distance. For typical experimental parameters (f = 100–1000 Hz, v = 0.1–1 mm/s, d = 0.03–0.04 mm, δy = 0.01–0.001 mm) $N \gg 1$.

The depth profile of the alloy is studied after the laser processing by means of XPS (*Axis HS, Kratos Analytical*). The XPS is designed for sensitive analysis of a sample surface compound; it collects information from the depth of several nanometers. In order to measure the sample chemical compound as a function of depth (in-depth profiling), the XPS device is integrated with ion gun for sample etching. As one can see in Fig. 1, the direction of the argon sputtering for the depth profile measurement is opposite to the direction of the laser beam propagation. The diameter of the XPS analysis area is 150 μm.

Comparative depth profiles of laser-treated and untreated layers have been recorded under the following conditions: excitation with non-monochromatic Mg Kα radiation, the hemispherical analyser was operating in the fixed analyzer transmission (FAT) mode, pass energy 80 eV under a take-off angle of 0° with respect to the surface normal.

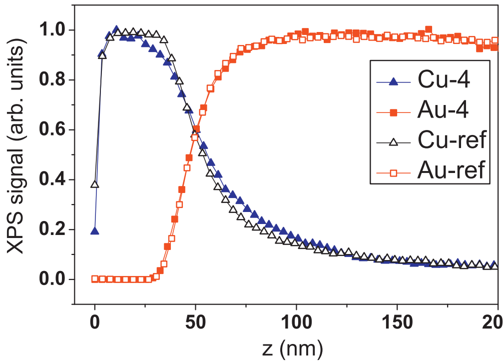

Fig. 2. XPS in-depth profiles for the 200 nm gold + 50 nm copper sample normalized to the maximum of the signal intensity; laser pulse fluence F = 7.7 kJ/m^2, overlap N = 225 pulses, pulse duration t_p = 0.12 ps. Solid triangles – copper profile after laser alloying, solid squares – gold profile after laser alloying, open triangles – copper profile before laser alloying, open squares – gold profile before laser alloying. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For the depth profile, spectral regions around Au 4f and Cu 2p$_{3/2}$ were measured with 0.2 eV per step. Alternating sputter cycles of 2 min were applied. Ar$^+$-Ions were used with energy of 3 keV, current of 250 nA and an angle of incidence of 45° with respect to the surface normal. The sputtered area was 2 mm × 2 mm. Under these conditions, the sputtering rate was 1.0 nm/min referred to Ta_2O_5.

In order to reconstruct the laser-induced interface changes, raw XPS intensities are plotted, see Fig. 2. The amplitude of the XPS signals is proportional to the number of atoms of specific metal in the surface volume defined by the beam area and the electron attenuation length [5]. The Y-axis scaling coefficients and the base lines for different measurements were adjusted in the plot to keep the signal amplitude unchanged far from the alloying area, since no mixing takes place there and the number of atoms should be kept unchanged.

3. Numeric simulations of laser-induced melting

Numeric calculations give a qualitative overview of the femtosecond laser induced melting and resolidification processes. Two-Temperature Model (TTM) simulations [9] describe evolution of the temperature and the melt fraction on the sample surface after the laser pulse is absorbed by the sample. The melt fraction can be calculated by comparing the melting enthalpy with the total energy left in a volume after it is heated up to the melting point.

The time-depth plot of the lattice temperature evolution in the studied sample shown in Fig. 3(a) is calculated in frames of one-dimensional TTM with temperature-dependent values of the electron–phonon coupling and electron heat capacity and thermal conductivity [10]. The laser pulse impacts the sample surface at the depth z = 0 at time t = 0. Penetration length for the laser radiation was chosen to be 16.3 nm; the penetration range of ballistic electrons in gold is 105 nm [11]. The energy transport by ballistic (or *runaway*) electrons is important since the electron penetration scale is comparable to the thickness of the gold layer. This fact as well as a higher electron–phonon coupling constant of copper, which is approximately 5 times larger than that of gold, result in a certain increase of the lattice temperature in the copper layer near the copper–gold interface. This effect has been recently reported in [12]. For certain pulse energies this may lead to formation of two independent melt zones: One is on the laser-faced sample surface, the other one is on the gold-copper interface, see Fig. 3(b).