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Heat effects of metals ablated with femtosecond laser pulses

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Abstract

Heat effects of metallic bulk crystals of Au, Ag, Cu, and Fe ablated with femtosecond Ti:sapphire laser pulses is experimentally studied. As a result of X-ray diffraction (XRD) measurements, the XRD peak signal of the area ablated with Ti:sapphire laser is much smaller than that of the crystalline metal sample. While the crystal form of the metal sample is crystalline before laser ablation, the crystal form in the ablated area is *partially* changed into the amorphous form. The residual pulse energy that did not contribute to the ablation process remains, which leads to the formation of thin layer of melted phase. The melted layer is abruptly cooled down not to be re-crystallized, but to transform into amorphous form. It is evident that the area ablated with femtosecond laser is changed into amorphous metals. This mechanism would be the same as the melt-quenching generally used as the fabrication method of amorphous metals. This experimental result is consistent with the theoretical result.

Keywords: Laser ablation; Femtosecond laser; Amorphous metal; Crystalline metal

1. Introduction

Significant advancement of tunable solid state lasers and the chirped pulse amplification technique by using Ti:sapphire, Cr:LiSAF and Cr:LiCAF laser media has led to a challenging phase of application research. The application fields opened up high-intensity physics [1], ultrafast chemistry [2], 3D non-linear imaging [3], ultrashort pulsed laser ablation [4,5], and so on. Ultrashort pulsed laser ablation is one of the most promising technologies among femtosecond laser applications, because the ablation physics is drastically different from those in conventional nanosecond pulsed laser ablation. Generally, the electron-lattice relaxation time in metals is 1–10 ps [6,7]. Therefore, the mechanism of femtosecond laser ablation is different from that of longer pulsed laser ablation. Thermal ablation occurs when the laser pulsewidth is longer than the electron-lattice relaxation time. The importance of the pulsewidth compared to the electron-lattice scattering time and the thermal diffusion time corresponding to the skin depth was pointed out by Stuart et al. [8]. In a wide band-gap insulator under strong laser irradiation, direct observation of multiphoton absorption by free electrons was reported [9]. Additionally, laser ablation of dielectrics with pulse durations between 20 fs and 3 ps has been investigated [10], and machining of sub-micron holes using a femtosecond laser at 88 nm has been demonstrated [11].

Moreover, femtosecond laser ablation of materials with high thermal conductivity is of paramount importance [12,13], because the chemical composition and properties of the area ablated with femtosecond laser is kept unchanged [13,14]. The material processing by femtosecond laser can well control the heat-affected

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zone of the dielectric materials. Regarding metal ablation, residual energy left in the metal, which is not used for ablation, will induce liquid phase, leading to the amorphous/polycrystalline phase of the metal during resolidification. The heat transfer in metals irradiated by sub-picosecond laser pulses is theoretically simulated based on the two-temperature diffusion model [15]. However, it is not *experimentally* demonstrated that the heat effects are induced by femtosecond laser pulses.

In this paper, we would like to report on the heat effects of metallic bulk crystals of Au, Ag, Cu, and Fe ablated with femtosecond Ti:sapphire laser. Due to the heat effects induced by laser pulses, the ablated bottom area is partially converted into the amorphous metals from the crystalline metals.

2. Experiments

The laser used in our experiments is a commercially available titanium–sapphire laser (Tsunami, Spectra Physics), with a chirped pulse amplification system (Split-fire, Spectra Physics) pumped by the second harmonic of a Nd:YLF laser at a 1 kpps repetition rate (Merlin, Spectra Physics). The pulsewidth, a center wavelength and pulse energy is 110 fs, 800 nm and 0.45 mJ, respectively. The intensity autocorrelator and the powermeter at the output of the amplifier periodically monitor the drifts of the pulsewidth and output energy in order to ensure a stable pulse energy on a target. To control the pulse energy, we used optical neutral density filters. Thus, the calibration parameter is confirmed prior to the ablation experiments. A 80 mm focal-length fused silica convex lens is used to focus the attenuated laser pulses onto the targets. The irradiation number of laser pulses is controlled by a mechanical shutter. Metallic bulk crystals used here are Au, Ag, Cu, and Fe. The thermal properties of Au, Ag, Cu, and Fe are listed in Table 1 [16]. All ablation experiments are performed in air at room temperature. In measurements, we use X-ray diffraction (XRD, Rigaku RAD-C) to observe the crystal form of the ablated area.

Table 1
The thermal properties of Au, Ag, Cu, and Fe [16]

	Thermal conductivity (W/m K)	Heat capacity ($\times 10^6$ J/m^3 K)	Melting point (°C)	Boiling point (°C)
Au	317	2.49	1064	2856
Ag	429	2.47	962	2162
Cu	401	3.45	1085	2562
Fe	80	3.53	1538	2861

3. Results and discussion

The dependence of the ablation rate on the laser fluence is investigated in order to characterize the ablation process. Fig. 1 shows the ablation rates of Au, Ag, Cu, and Fe. Ablation depth, measured using a mechanical stylus (Dektak-3030). The estimated ablation rate is an average value of 300 laser shots. In the case of Au, Ag, and Cu ablated with Ti:sapphire laser, it is observed that the ablation rate has two different ablation regimes, as reported by Nolte et al. [17] and Furusawa et al. [12]. The characteristic depth of the two different ablation regimes is explained by the optical skin depth (penetration depth) and the thermal diffusion length, which is determined by the peak electron temperature in the framework of the two-temperature model. However, it is not found for Fe that there are two ablation regimes like other metals, because of the small thermal conductivity of Fe.

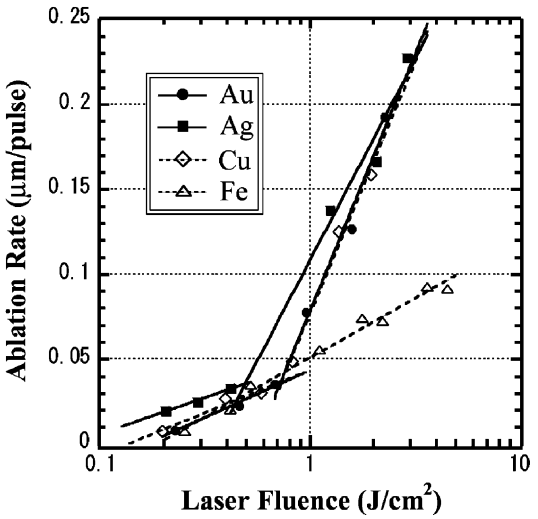

Fig. 1. Plots of ablation rate per pulse as a function of Ti:sapphire laser fluence for Au, Ag, Cu, and Fe.

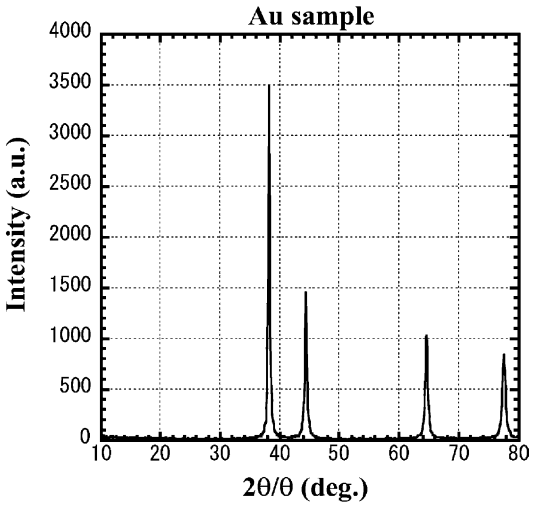

Fig. 2. XRD signals of Au sample before laser ablation.

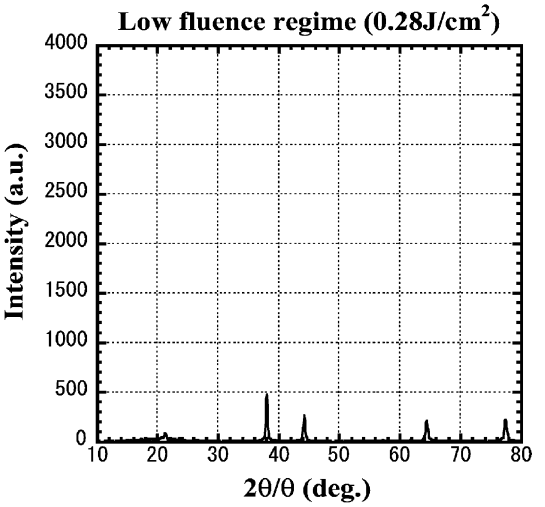

Fig. 4. XRD signals of Au after laser ablation. The laser fluence is 0.28 J/cm^2.

Therefore, we perform ablation experiments for three laser fluences (below the threshold fluence, low fluence regime, and high fluence regime) determined by each metal. After that, the crystal form of the ablated area is measured using XRD.

As a result of XRD measurements, the XRD peak signals of the bottom area ablated with Ti:sapphire laser is found to be much weaker than that of the crystalline metal sample, as shown in Figs. 2–5. Although these figures show the XRD signals of Au, the same results are obtained in the case of other metals as well. However, Fe has different ablation rate from other three metals, and the XRD peak signals of the ablated area is weaker than that of the crystalline sample. Although the crystal form of the metal sample used is crystalline before the laser ablation, the crystal form after the ablated area is *partially* changed into the

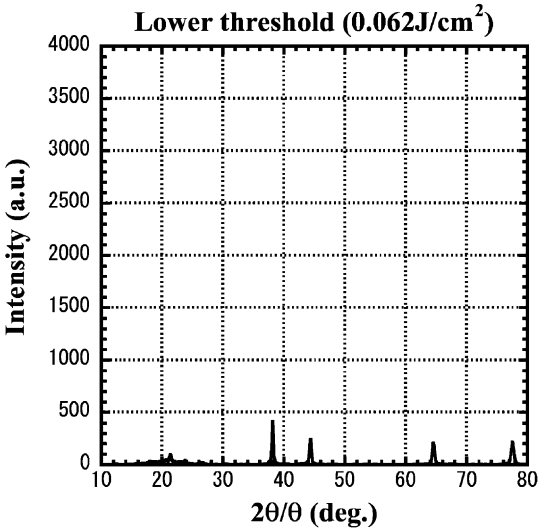

Fig. 3. XRD signals of Au after laser ablation. The laser fluence is below the threshold fluence of 0.062 J/cm^2.

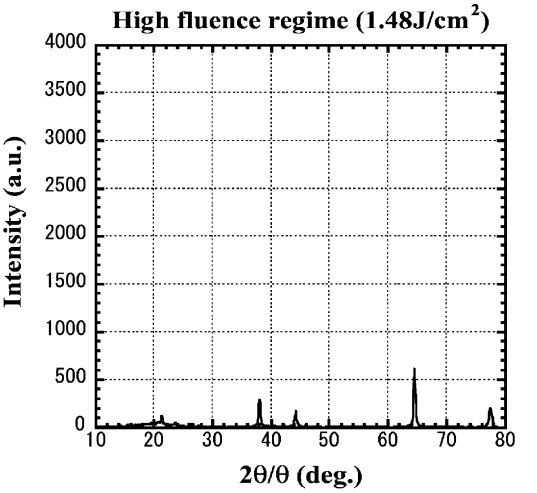

Fig. 5. XRD signals of Au after laser ablation. The laser fluence is 1.48 J/cm^2.

Table 2
Absorption coefficients and skin depths of metals at respective wavelengths

	At 0.15406 nm (the wavelength of X-ray of XRD)		At 800 nm (the wavelength of Ti:sapphire laser)	
	Absorption coefficient (cm^{-1})	Skin depth (μm)	Absorption coefficient (cm^{-1})	Skin depth (μm)
Au	4006	2.50	7.25×10^5	0.0138
Ag	2290	4.37	9.21×10^5	0.0109
Cu	460	21.7	8.36×10^5	0.0120
Fe	2396	4.17	5.72×10^5	0.0175

amorphous form. The residual laser energy absorbed that did not contribute to the ablation process remains, leads to the formation of thin layer of melt phase. The melt layer is abruptly cooled down not to be re-crystallized, but to be amorphous. It is evident that the area ablated with femtosecond laser is converted into amorphous metals. This mechanism would be similar to the melt-quenching generally used as the fabrication method of amorphous metals. This experimental result is consistent with the theoretical results reported by Furukawa and Uchida [18] who performed the simulation of metal ablation by femtosecond laser and found to form the melted layer at the ablated area. While the XRD signal of the complete amorphous material has no peak, the results we obtained show weak peak signals. The optical absorption coefficient of metals at 800 nm of Ti:sapphire laser is much larger than that at the wavelength of X-ray we used to measure, as listed in Table 2 [16]. Because the energy of Ti:sapphire laser is absorbed only by very thin portion near the surface, that area changes into amorphous from the crystal form after laser ablation. Therefore, the results of small peak signals are obtained by XRD measurement, because the crystalline part under the amorphous layer changed by laser ablation is also measured.

4. Summary

Heat effects of metallic bulk crystals of Au, Ag, Cu, and Fe ablated with femtosecond Ti:sapphire laser pulses is experimentally studied. As a result of XRD measurements, the XRD peak signal of the area ablated with Ti:sapphire laser is much smaller than that of the crystalline metal sample. While the crystal form of the metal sample is crystalline before laser ablation, the crystal form in the ablated area is *partially* changed into the amorphous form. The residual pulse energy that did not contribute to the ablation process remains, results in the formation of thin layer of melt phase. The melt layer is abruptly cooled down not to be re-crystallized, but to transform into amorphous form. It is evident that the area ablated with femtosecond laser is changed into amorphous metals. This formation mechanism would be the same as the melt-quenching generally used as the fabrication method of amorphous metals.

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