# Laser-induced Preparation, Laser Melting, and Laser Cleaning of Chromium Microparticles

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Chromium microparticles (20–100 nm) were prepared by 248– nm laser irradiation of deaerated aqueous solutions of chromium (II) dichloride in the presence of sodium formate and sodium polyphosphate, followed by aging. The microparticles transferred onto a silicon substrate were melted by 193– nm laser irradiation. The microparticles on a silicon substrate could be almost completely removed by 308– nm irradiation at the fluence of 0.5 J $cm^{-2}$ $pulse^{-1}$.

Metal microparticles attract much current attention of physicists and chemists. They also have a broad range of industrial application such as catalysts, etc. In particular, chromium microparticles are very important in view of its potential for photomask repair and photomask pattern making. Laser-induced reduction of metal ions in aqueous solutions provides a very convenient means for microparticle preparation, as already reported for silver colloid particles by one of the authors.[1] On the other hand, laser-induced vaporization or ablation constitutes a very efficient way of surface cleaning, removing particle contaminants from solid surface.[2] In the present report, excimer laser irradiation at 248, 193 and 308 nm is shown to work for preparation, melting, and removal of chromium microparticles, respectively. Chromium microparticles are prepared for the first time to the best of our knowledge.

(1) Laser induced preparation of chromium microparticles. Preparation of silver microparticles using γ-ray of $^{60}Co$ or high-energy electron beam has been reported by Henglein's group[3–5] and Belloni's group.[6,7] Henglein et al. reported formation of cadmium[8] and lead[9] microparticles. Chromium is a very important metal in photomask repair. However, direct reduction of $Cr^{3+}$ to $Cr^0$ is not feasible in view of the large negative standard electrode potential.[10]

$$Cr^{3+} + 3e^- = Cr : -0.710V. \quad (1)$$

Reduction of $Cr^{2+}$ ion is feasible, however, since (1) and

$$Cr^{3+} + e^- = Cr^{2+} : -0.410V, \quad (2)$$

lead to

$$Cr^{2+} + 2e^- = Cr : -0.300V, \quad (3)$$

which is less negative compared to cadmium.

$$Cd^{2+} + 2e^- = Cd : -0.402V.$$

Aqueous solutions typically containing $CrCl_2$ ($8.0\times10^{-4}$ M), HCOONa ($2.0\times10^{-4}$ M), $(NaPO_3)_m$ ($2.5\times10^{-4}$ M), and NaOH ($2.0\times10^{-4}$ M) were prepared under nitrogen atmosphere. The solution was degassed in an glass ampule connected to a 1 cm×1 cm quartz cell. The solution was transferred to the cell, irradiated with 248– nm light (5 Hz, typically 14 mJ $cm^{-2}$ $pulse^{-1}$) from a Lambda Physik LPX105 excimer laser. The irradiated solution was aged at room temperature for 1–3 h. After aging colloid solution was pipetted onto a quartz or a silicon substrate in the air. After vacuum drying, water-soluble components were dissolved away by distilled water. Water was vaporized off. Microparticles obtained on a quartz or a silicon substrate were observed with SEM using a Hitachi S-2300 scanning electron microscope. An example of SEM images of microparticles is shown in Figure 1. Aggregated particles consisting of small microparticles with a diameter of 20–100 nm can be seen. EDX on a silicon substrate (Figure 2a) shows that only chromium was present. ESCA data, after elimination


**Figure 1.** SEM image of chromium microparticles (Initial solution: $8.0\times10^{-5}$ M Cr; 248– nm laser irradiation: 5 Hz, 14 mJ $cm^{-2}$ $pulse^{-1}$, 1500 pulses; aging: 3 h at 23 °C).

of native oxide (showing a peak at 578.16 eV corresponding to Cr $^2p_{3/2}$) by argon etching, manifest a peak at 576.22 eV (see Figure 2b), which is very close to 576.0 eV for $Cr^0$.[11]

Threshold concentration of particle formation. Several initial solutions containing $8.0\times10^{-8}$–$8.0\times10^{-5}$ M of chromium (II) salt were prepared. (Concentrations of other reagents were changed in proportion to that of chromium salt throughout in this study.) These solutions were irradiated for 5 min (i.e., 1500 pulses). After aging for 3 h at 23 °C, relative amount of microparticles was judged from the area covered by particles in each SEM image. The result tells that the amount increased with Cr concentrations in the initial solutions with a threshold near $1\text{–}2\times10^{-7}$ M under these irradiation conditions.

Numbers of 248– nm laser pulses necessary for particle formation. Initial solutions containing $8.0\times10^{-7}$ M Cr were irradiated with 1, 10, 50, 100, 150, 300 and 1500 pulses of 248–nm laser light (5 Hz, 17.5–25.0 mJ $cm^{-2}$ $pulse^{-1}$). From SEM images after aging for 3 h at 23 °C it was shown that ten pulses could produce some microparticles, and no significant increase in the amount of particles was found after 100–150 pulses.

Aging time and aging temperature. Using initial solutions containing $8.0\times10^{-4}$ M Cr irradiated with 3000 pulses of 248–nm laser light (5 Hz, 14 mJ $cm^{-2}$ $pulse^{-1}$), aging was performed

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at 5 °C, 23 °C, and 45 °C. Droplets of sample solutions were taken out after 30 min, 1 h and every hour up to 8 h of aging. SEM images tell the following. For aging at 23 °C, microparticles were observed already after 30 min, and they grew with aging time. A similar result was obtained for aging at 45 °C. Growth of microparticles was remarkably slow at 5 °C, however.

(2) Laser melting of chromium microparticles. Chromium microparticles prepared as before and transferred onto a silicon substrate were irradiated with 193- nm laser light from a Lambda-Physik LPX-105 excimer laser (5 Hz, 60 mJ $cm^{-2}$ $pulse^{-1}$, 100 pulses). Results shown in Figure 3 tell the occurrence of extensive melting-resolidification. This is important to obtain uniform, smooth surfaces of chromium microparticle aggregates and to integrate these aggregates with underlying photomask frame in practical applications.

(3) Laser-induced removal of chromium microparticles from

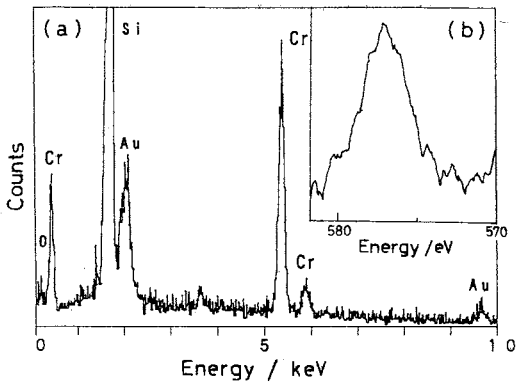


**Figure 2.** (a) EDX result on a Si substrate. Peaks of Cr are found at 0.5, 5.3 and 5.9 keV. The peak at 1.7 keV is due to Si, those at 2.1 and 9.7 keV are due to Au used for gold sputtering. (b) ESCA spectrum after Ar etching.

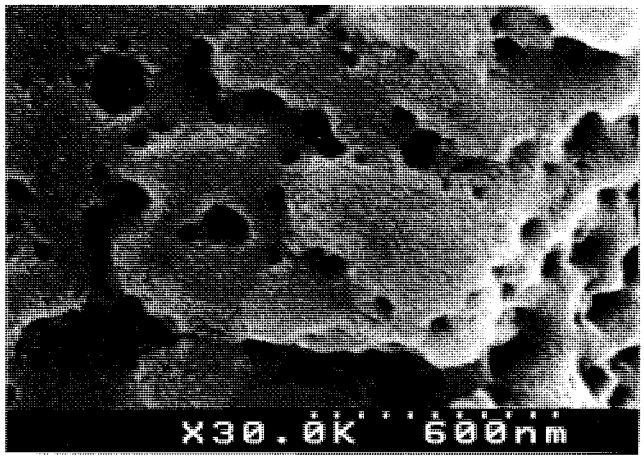


**Figure 3.** Laser melting-resolidification. 193- nm laser irradiation (5 Hz, 60 mJ $cm^{-2}$ $pulse^{-1}$, 100 pulses).

silicon and quartz substrates (laser-cleaning). Chromium microparticles on a silicon substrate were removed under irradiation with 100 and 1000 pulses of 308- nm laser light from a Lambda Physik LPX-105 excimer laser at the fluence of 0.5 J $cm^{-2}$ $pulse^{-1}$. Microparticles decreased in number by 100 pulses and were removed almost completely by 1000 pulses. 308- nm irradiation at 0.1 J $cm^{-2}$ $pulse^{-1}$ was not enough; many microparticles remained even after 6000 pulses. At 1.0 J $cm^{-2}$ $pulse^{-1}$ significant removal was observed even by 10 pulses, and almost complete removal occurred by 100 pulses. The irradiation at this fluence, however, accompanied ablation of silicon substrate surface. Incidentally, ablation threshold of silicon was found to be 0.7-1.0 J $cm^{-2}$ $pulse^{-1}$, in good accordance with Larciprete's result[12] of laser cleaning of silicon (100) surface with 248-nm light. Results of laser-induced removal of chromium particles from a quartz substrate with 308- nm irradiation (0.5 J $cm^{-2}$ $pulse^{-1}$, 1000 pulses) are shown in Figure 4. In this case, the left half of substrate was masked and hence not irradiated. Boundary of cleaned and noncleaned area is very sharp.

We have used three wavelengths (193, 248, and 308 nm) in this study. Laser induced preparation of chromium microparticles, performed with 248- nm light, could have been done by a higher-energy photon (193 nm). However, we made use of higher fluence of the 248- nm light. Laser cleaning could be

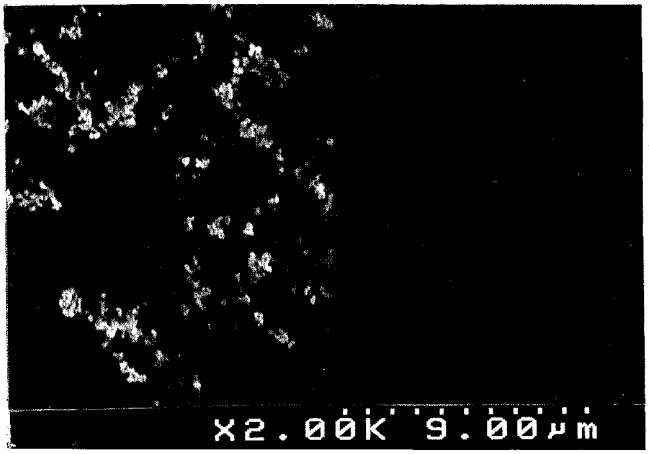


**Figure 4.** Laser cleaning on a quartz substrate, half masked, by 308- nm laser light (5 Hz, 0.5 J $cm^{-2}$ $pulse^{-1}$, 1000 pulses).

made with 248- or 193- nm light. The 308- nm light was chosen to minimize the damage to the underlying solid substrate.

In conclusion, excimer laser light at 248, 193 and 308 nm can be used for preparation, melting, and removal (evaporation) of chromium microparticles, respectively. This finding has a significant merit in practical application in photomask repair and photomask pattern making.

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