Femtosecond laser induced surface melting and nanojoining for plasmonic circuits

A. Hu*a,b, G. L. Dengb, S. Courvoisieerb, O. Reshefb, C. C. Evansb, E. Mazurb, Y. Zhoua
aDepartment of Mechanical and Mechatronics Engineering and Centre of Advance Materials of Joining, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada
bSchool of Engineering and Applied Science, Harvard University, 9 Oxford Street, Cambridge, Massachusetts, 02138 USA

ABSTRACT

Femtosecond laser induced nonthermal processing is an emerging nanofabrication technique for delicate plasmonic devices. In this work we present a detailed investigation on the interaction between ultra-short pulses and silver nanomaterials, both experimentally and theoretically. We systematically study the laser-silver interaction at a laser fluent from 1 J/m² to 1 MJ/m². The optimal processing window for welding of silver nanowires occurs at fluences of 200–450 J/m². The femtosecond laser-induced surface melting allows precise welding of silver nanowires for “T” and “X” shape circuits. These welded plasmonic circuits are successfully applied for routing light propagation.

Keywords: Femtosecond laser, silver nanomaterials, nano-thermal processing, plasmonic circuits

1. INTRODUCTION

Nanofabrication based on the nanojoining method has attracted extensive interests since the E-beam lithography has limitations to develop nano-circuitry and nanoelectronics [1-4]. Not only E-beam lithography is difficult to write a nanowire with a single crystal structure and the atomic flatted surface, it is also challenge to fabricate nanodevices with 3 dimensional structure and hybrid materials using E-beam lithography [5]. Current E-beam lithography involves many steps including thin film deposition, resist masking, E-beam writing, etching, lift-up, it is almost impossible to develop an atomic flatter surface [5]. For a nanoscale light waveguide, single crystal structure and ultra-smooth surface is required to reducing the dissipation [3]. For basic nanoelectronics, the assembly of an architecture based on different building blocks is critical for proper functions and applications [6].

Sintering is a basic joining manufacturing which results in a density-controlled material starting from powder materials. At a microscale, sintering is a thermal activated mass transfer procedure driven by the surface energy and total curvature of two neighboring particles. At a nanoscale, due to a higher surface and the size effect, the solid state diffusion can occur at very low temperatures, even at room temperature [7,8]. However, a liquid phase sintering is expected as a more time-effective procedure than a solid state sintering since a liquid phase sintering takes place at a higher temperature than a solid state sintering. Recently, our theoretical study based on molecular dynamics simulation unveiled that a surface melting can occur at a rather lower temperature than the particle melting temperature [9] although the particle melting is lower than the bulk melting temperature due to the size effect [10]. This clearly shows that the melting and thereby the liquid phase sintering are the significant factors to be considered during nano-manufacturing.

For the joining at a nanoscale, the activated energy should be highly localized to avoid the negative effect on the building blocks. Various energy sources have been employed for nanojoining. Nanosoldering in heated liquid medium is one of popular but less controlled joining methods [11]. A tip-style solder carrier can transfer pico-letre solder and implement microscopic interconnection on a hotplate with the aid of optical microscope [12]. A microscale ultrasonic
Femtosecond laser irradiation provides a powerful tool for nanosintering since the interaction between femtosecond laser pulses and materials involves ultrafast electron excitation, nonthermal melting and nanoscopic surface morphology modification [4, 18, 19]. Although a two-temperature model was used to describe the energy transferring procedures [18, 19] nanomaterials display the significant size and shape effects on their thermodynamic, chemical and optical properties, which may result in remarkable differences from the features shown in bulk processing [19]. It is long known that a nonthermal melting of bulk occurs under bombardment of extremely intense laser pulses [4, 20]. Our recent work shows that silver nanoparticles can be joined at an influence at least 2-order lower than the bulk damaged threshold [4, 21]. This indicates that the relative thermodynamic processing, such as melting and sintering at a nanoscale needs to be revisited. Furthermore, for a silver nanowire, in which the incident laser energy will be re-distributed through surface plasmon excitation and propagation the feasibility and underlying mechanisms of femtosecond laser irradiation are worth systematic study [22].

In this work we compared two kinds of nanojoining techniques, namely, thermal nanosintering and femtosecond laser nanosintering. A surface melting is evident in femtosecond laser irradiation. Such a surface melting allowed to join two adjacent nanowires at an arbitrary angle, which highlighted the potential application in developing plasmonic circuits and even more complicated plasmonic devices with 3D architectures.

![SEM images of silver nanowires at room temperature and annealing at different temperatures](image-url)

Fig. 1 SEM images of silver nanowires at room temperature and annealing at different temperatures
2. EXPERIMENTAL PROCEDURE

Ag nanowires were prepared in a AgCl seeded solution with PVP as a structure directing reagent using a method modified from the literature [8, 23]. The as-grown Ag nanowires were washed for two times with ethanol and deionized water, alternatively, and subsequently recovered from solution with centrifugation. The cleaned wires of 10-30 μm long with an average diameter of 100 nm were dispersed in deionized water and deposited on Si wafers for investigation. For a comparison, silver foils were mechanically polished down to 0.2 μm with alumina paste.

The thermal processing was carried on with a hotplate. The laser processing was conducted with a 35 fs 800 nm Ti:sapphire laser system at a repetition rate of 1 KHz. The laser power was attenuated with rotating a polarizer relative to a wave-plate with half wavelength. The focal area was measured with a CCD camera and a photography imaging software after attenuated the laser power. The light paths to the camera and to the focal point on the sample surface were kept at the same lengths. All processing were completed in air.

The morphology of silver nanowires was characterized with high resolution optical microscope (Nikon Ti-e) with an oil-immersion lens (x63, numerical aperture 1.4), scanning electron microscopy (SEM, Zeiss Ultraplus) and transmission electron microscope (JOEL 2010F). The profile of irradiation crater was measured by a profilometer. The optical properties were measured with UV-NIR and Raman spectrooscope.

3. RESULTS AND DISCUSSIONS

[1] Thermal nanosintering

Fig. 1 shows silver nanowires at a room temperature and annealed at different temperatures. At room temperature a polymer layer with a thickness of 3-5 nm is observed to be coated on the surface of silver nanowires. The removing of this passive layer will lead to the end-to-end joining of nanowires at room temperatures [24]. Shown in Fig. 1 the nanowires crossly overlap but not joined. A transporting measurement shows that the contacting resistance is about a few MΩ, consistent with the existence of the surface polymer layer. At 150°C for 10 min the overlapped wires start to join. At 200°C for 10 min, the overlapped wires clearly joined together. The joining forms both “X” and “T” shapes. However, at 250°C for 10 min, nanowires broke, melt and formed some short bars and nanoparticles. These results are similar to a plasmonic heat through a strong light source, where the thermal effect causes the melting and the shape change of silver nanowires [25]. It is evident that the thermal nanosintering will dramatically change the shape of nanowires and thereby modify the plasmonic properties.


Fig. 2 shows femtosecond laser irradiation of silver nanowires deposited on Si wafer. At an energy density higher than 1130 J/m² the nanowires are melting and partially vaporized. The melt parts are welded together. At an intermediate energy density of 560 J/m² the nanowires are partially melting. The joining is evident between large nanoparticles and...
neighboring nanowires. At an appropriate energy of 300 J/m², only the surface melting is evident. The touching nanowires are nicely joining without dramatically changing the shape. As mentioned in the introduction, such a nanojoining is critical to build plasmonic circuits. At an energy intensity lower than 200 J/m², no joining is evident at overlapped nanowires.

![Image of polished silver foils](image)

Fig. 3 Surface morphology of polished silver foils irradiated by femtosecond laser at an intensity of 3x10⁵ J/m² for 10 pulses. (c) the center of the irradiated crater. (M) the intermediate regime. (E) the edge area.

[3] Surface melting

To elucidate the interaction mechanism between femtosecond laser and nanomaterials we revisited the irradiated effect of polished silver foils. Shown in Fig. 3 is the irradiated effect of femtosecond laser pulses. In the center of damaged area, cellular structures are clearly observed with the solidification of liquid drops. The melting is evident. In the intermediate regime, both particles and cellular structures are observed. The particle size are quite scattered and ranged from tens nanometers to submicrometers. At the edge area, the typical features are submicrometer particles with tiny nanoparticles on the particle surface and on the substrate surface. These tiny nanoparticles may come from the surface melting.

Fig. 4 shows that the damaged depth of polished silver foils as a function of laser intensity. It is clear that the laser intensity dependence of the depth is approximately a semi-log function. The solid line is a fit based on two-temperature model, \( L = \alpha^{-1} \ln(F/F_{th}) \), with \( \alpha^{-1} \) as the electron thermal penetration depth and \( F_{th} \) the damage threshold [18]. The best fitting yields \( \alpha^{-1} = 218 \) nm and \( F_{th} = 18400 \) J/m². This damage threshold is slightly lower than the damage value of silver films at 30000 J/m² for a nanosecond pulse. Meanwhile, the thermal penetration depth is also approximately equal to the average size of nanoparticles. It is notable that at a lower energy intensity the femtosecond laser irradiation displays a surface processing with a skin thickness less than 50 nm. However, the processing energy intensity windows for nanosintering of silver nanowires and nanoparticles locate in the range at least 1-2 order lower than the damage threshold. This demonstrates that femtosecond laser can induce the surface melting at the very low energy range. This
surface liquid phase dramatically facilitate the nanosintering. However, the surface melting mechanism induced by femtosecond laser irradiation is worth further study.

![Graph showing damaged depth as a function of laser energy for polished silver foils. The red line and the blue line stand for the processing regimes of silver nanowires and silver nanoparticles, respectively.]

**Fig. 4** shows the damaged depth as a function of laser energy for polished silver foils. The red line and the blue line stand for the processing regimes of silver nanowires and silver nanoparticles, respectively.

### 4. CONCLUSIONS

In this work, we display the successful nanojoining of silver nanowires induced by femtosecond laser irradiation. The thermal effect by femtosecond laser processing is precisely limited within the surface with tens nanometer thickness. Thus, our results show that it is feasible to develop nanocircuits based on femtosecond laser induced surface melting and nanojoining.

### 5. ACKNOWLEDGEMENT

This work is supported by the Canadian Research Chairs (CRC) program, National Sciences and Engineering Research Council (NSERC) and the National Science Foundation, USA.

### REFERENCES


