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Solid–liquid–solid process for forming free-standing gold nanowhisker superlattice by interfering femtosecond laser irradiation

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ABSTRACT

One-dimensional nanomaterial superlattices are fundamental components in plasmonics, nanophotonics, and nanoelectronics. Bottom-up techniques such as vapour–liquid–solid (VLS) and chemosynthesis have been used to fabricate the structure but are nonoptimal for controlling alignment and size. Here we report the fabrication of gold nanowhisker superlattice, based on a novel mechanism termed solid–liquid–solid (SLS). An interfering femtosecond laser pulse induces fluid flows of nanosize gold, which is followed by droplets pinching off from them and freezing of a free-standing nanowhisker superlattice fixed on a substrate. The shape is defined by liquid motion and not by crystallographic growth although its structure is polycrystalline. The smallest curvature radius of its vertex was 3.4 nm, which is one-half of the smallest nanorods fabricated by chemosynthesis. SLS process is a superior alternative to sequential bottom-up processes involving catalyst fabrication, bottom-up synthesis, purification, alignment, stabilization, and preservation.

1. Introduction

Metallic nanomaterials with high-aspect-ratio structures have wide potential in plasmonics, nanophotonics, and nanoelectronics, including use in optical antennas for surface-enhanced Raman scattering (SERS) detection [1], metamaterials exhibiting a negative index or permeability [2,3] plasmonic devices [4,5]. Crystalline 1D nanomaterials have been grown by bottom-up techniques such as the vapour–liquid–solid (VLS) mechanism [6,7], co-reduction in an aqueous solution of acid and chloroauric acid [4], and seed-mediated growth in solution [8]. These methods have narrow process windows, are not versatile to different materials, and require extra preservation (e.g. addition of a surfactant) to avoid nanoscale cold welding and aggregation [9,10]. In addition, alignment of 1D nanomaterials is critical to induce or enhance magnification and tune interaction between electromagnetic and plasmonic waves [2,3,5]. Therefore, a pre-process for fabricating catalytic template in a lattice has been developed, along with a post-process manipulation. In the pre-process, a lattice template can be formed by self-organization of nanoparticles [1,11] or by lithography. In the former technique, the lattice period depends on the particle size and fluctuates because of size dispersion. Lithography supplies an accurate lattice but is time and cost consuming [2]. Post-process manipulation is impractical for mass production.

2. Solid–liquid–solid process

Interference patterns for lasers improve lattice accuracy and have been applied to writing Bragg grating [12] and distributed-feedback lasers [13]. Direct processing of material by use of interference patterns has been attempted, but it is difficult for longer-pulse lasers because of thermal diffusion, which levels the energy distribution induced by the interference pattern. It has been successful only for photo-dissociative polymers irradiated by a UV interference pattern, in which a periodic groove was dug by a few hundred pulses of a laser [14]. On the other hand, ultrashort pulse laser processing has been investigated as a microprocessing tool for over two decades [15,16]. Although it has been assumed as a nonthermal processing technique, we found that a single pulse of a near-infrared femtosecond laser can induce nanosize fluid flow and inflate a thin gold film, in which the positions overlie the interference pattern, and the nanobump superlattice was frozen synchronously [17,18]. We denote this mechanism as a solid–liquid–solid (SLS) mechanism, in contrast to the VLS mechanism, as explained by Fig. 1. Initially, energy is induced into a thin film according to an interference pattern of multibeams, as explained by the sketch at the top-right of Fig. 1. At a spot on

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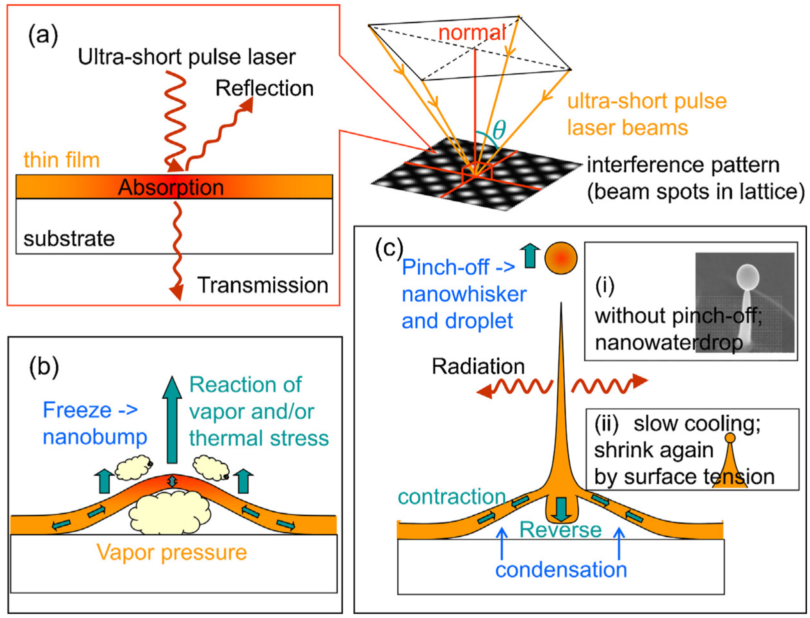

Fig. 1. Schematic of SLS process. Energy is periodically induced into metallic thin film according to an interference pattern of ultrashort pulse laser beams, as explained by the sketch at top-right. At a spot in the interference pattern: (a) induction of energy into a localized region results in a partial thermal process, (b) a part of the solute film is evaporated and launched by reaction of vapour pressure and/or thermal stress, and (c) formation of a droplet by surface tension, and a spiky structure is formed by pinching off this droplet and quick freezing.

the interference pattern, energy is induced into a localized region, which results in partial liquid motion of the solute metal thin film as shown in Fig. 1a. Vapour pressure and/or thermal stress of the solute metal can be the driving force for the motion, as explained in Fig. 1b [19]. The gold solute exhibits similar behaviour in a simulation where only thermal stress is considered [20], but water liquid exhibits similar behaviour with cavitation bubble generated by fs laser [42]. Now the contribution ratio of these mechanisms in the experimental condition in this paper is still under question. Here, the behaviour of the metal liquid is analogous to the motion of a water solution, captured by a high-speed CCD camera [21,22]. The behaviour of the water solution is controlled by factors such as flow speed and size, which correspond to the laser energy and lattice parameter in our process. For example, the types of unit gold nanostructures processed by our technique were spike on bump or nanocrown with lattice period of 1.7 μm or 3.9 μm, respectively [23,24]. The thickness and viscosity of solution correspond to target structure and temperature in our process. Under optimal conditions, a metal droplet forms on top of a liquid by surface tension and undergoes pinch-off, and a nanowhisker freezes. There are some exceptions to this process: if the kinetic energy of liquid motion is low, the droplet remains on the vertex, and a nanosize water drop is formed as shown in Fig. 1c(i) [17,18]; on the other hand, if the heat capacity is too large, it shrinks again after pinch-off as illustrated in Fig. 1c(ii); if the film is too thin, all of the material in the spot is evaporated and only a hole is formed. In this paper, we show nanosize

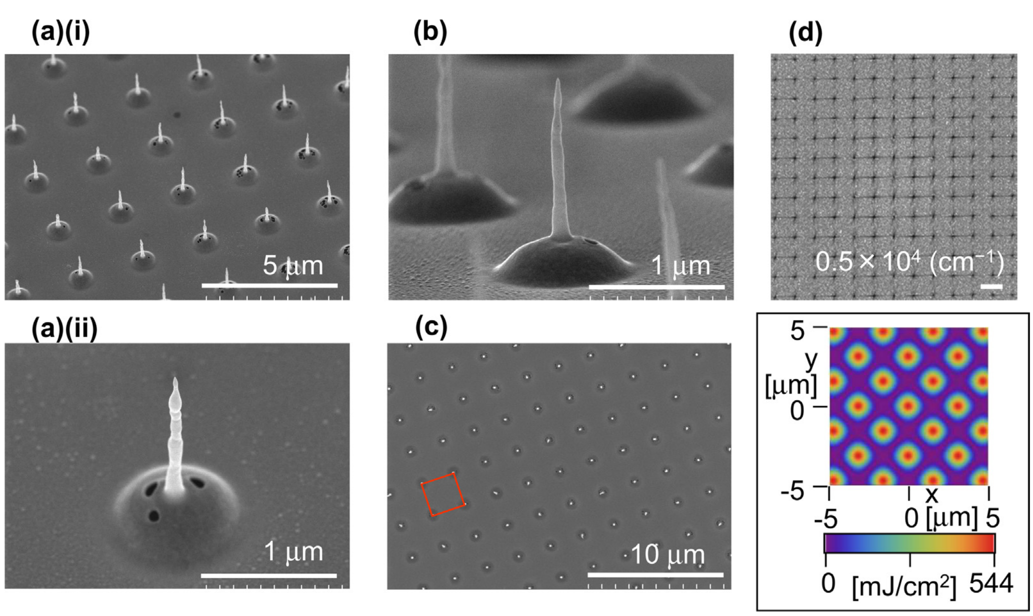

Fig. 2. Gold nanowhiskers superlattice. Observation at different oblique angles with (i) normal magnification and (ii) higher magnification, (a)–(c). 2D FFT image of 21 × 21 nanowhiskers, and (d) partly reflecting the top view shown in (c). Lower right inset is a simulated interference pattern, and the average fluence was 136 mJ/cm^2.