A nanoscale machine shop for Nanowires

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ABSTRACT

One-dimensional nanomaterials have attracted a great deal of research interest in the past few decades due to their unique mechanical, electrical and optical properties. Changing the shape of nanowires (NWs) is both challenging and crucial to change the property and open wide functions of NWs, such as strain engineering, electronic transport, mechanical properties, band structure, and quantum properties, etc. Here we report a scalable strategy to conduct cutting, bending and periodic straining of NWs by making use of laser shock pressure. 3D shaping of silver NWs is demonstrated, during which the Ag NWs exhibit very good ductility (strain to failure reaches 110%). Meanwhile, the high electrical conductivity of Ag NWs could retain well under controlled laser shock pressure. The microstructure observation indicates that the main deformation mechanism in Ag NWs under dynamic loading is formation of twinning and stacking fault, while dislocation motion and pile-up is less obvious. This method could be applied to other semiconductor NWs as well.

Keywords: laser shock, pattering, shaping, strain engineering, nanowires

With the ever-growing research development in NW synthesis [1-2], more and more research interest have been focused on post-processing of NWs, such as bending [3-4], buckling [5-6] and cutting NWs [7-8]. Inducing controllable forming of NWs provides important means for fundamental study in strain engineering, electronic transport, mechanical properties, band structure, and quantum properties, etc. As interconnects or other basic building blocks in the fields of nanoelectronics, nanoactuators, nanoresonators, and nanosensors [9-10], NWs with tunable shape are able to accommodate to various surface structure requirement, such as flexible electronics. In addition, studies have also shown that mechanical forming in NWs may change the electrical, optical and chemical properties of the NWs [5,11-12], providing many opportunities for developing new generation of NWs based devices.

However, despite the importance of controlling the size and shape of NWs, there are very limited methods for scalable shaping of NWs. Although forming and machining are common processes to change bulk metallic component into desired shape, it is still a great challenge in nano world. Currently, AFM tips are often used to apply forces to on the NWs in order to measure their mechanical properties. Single AFM tip has been used to push NWs lying over a trench [13], and two AFM tips can be used to hold and bend NWs [3]. However, AFM tip cannot be used to manipulate NWs practically since only one NW can be treated at a time and not feasible to generate complicated shape changes. Therefore, there is a need to develop scalable nanomanufacturing processes that can effectively form and machine large quantity of NWs to open wide applications of NWs.

Here we present a way to flexibly shape NWs in a scalable and controllable manner. The schematic setup is shown in Figure 1. A nanosecond pulsed laser is used as the energy source to irradiate the target, which sequentially consists of a confinement layer (glass), an ablative coating layer (graphite), an ultrathin metal foil, an elastomeric material layer, aligned NWs and a silicon nanomold [Figure 1(a)]. The silver NWs are coated on the lower side of the elastomeric material or the surface of the mold from ethanol suspension by dip coating, with larger portion of the NWs tend to align in the direction of pulling. When the laser pulse transmits through the confinement and ablates the ablative coating, the ablative coating quickly vaporizes and ionizes into plasma [Figure 1(b)]. The expansion of the plasma is confined and bounced off by the confining media, generating a strong shock wave, which provides a sufficient momentum to shape the metal foil and thus the underlying NWs onto the mold. It is important that the metal foil flows into the mold cavities because it provides conformal contact between metal foil and NWs, ensuring effective pressure to transfer from the metal foil to the NWs. In order to prevent damage of the NWs, a layer of elastomeric material is coated on the metal foil, which absorbs the shock energy. By adjusting process conditions, such as laser intensity, substrate (mold) material and mold shape, four different types of forming results: conformal shaping, uniform bending, cutting and lateral compression, have been successfully achieved on silver NWs. The flexible shaping ability makes this method an effective tool to fulfill different requirement of configuration of NWs in different applications. This technique provides a new way for scalable processing of NWs, in that nano-scale forming could be successfully induced in a large quantity of NWs lying over a macro-scale area (mm) in a one-step operation.

Controllable forming of NWs also enables fundamental study of mechanical response and structure evolution of NWs under dynamic shock loading, especially at the plastic range, which was majorly studied by numerical simulation due to the lack of experimental approaches. MD simulation has been used widely to study the deformation behavior of NWs in both elastic and plastic region [18-19], but the results are rarely verified because of ultrahigh strain rate (normally > 10^7 s^{-1}) in the simulation. The underlying mechanisms for the observed deformation behavior of silver NWs will be discussed.

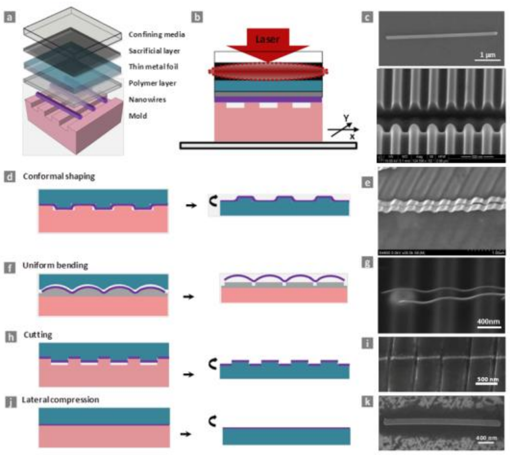

Figure 1 Laser shock based controllable forming of NWs.

In this study, the shaping of NWs can be controllable by adjusting the applied pressure induced by laser shock. the magnitude of laser shock pressure is determined by the laser intensity, shock impedance of the confining media and ablative coating, absorption coefficient of laser energy in plasma generation, and plasma layer thickness[20]. The laser intensity used in this study ranges from 0.07 to 0.2 GW/cm^2, and the calculated laser shock pressure ranges from 400 to 1000 MPa. Note that the laser shock pressure is that applied on the metal foil. The resulted magnitude of pressure applied on the NWs is further reduced by the elastomeric layer coated on the metal foil, which absorbs the shock energy.

This method is also flexible in forming types. By adjusting the mold shape, size and material used, four types of forming results have been achieved on an original straight and smooth silver NW [Figure 1(c)]. Figure 1 (f-k) depicts the schematic processes and typical forming results of the different forming types, which are conformal shaping, uniform bending, cutting and lateral compression, respectively. Among these four cases, conformal shaping is a basic type, which is obtained by using a rigid mold with low aspect ratio features [Figure 1(d)]. It can be seen that the silver NWs goes into the mold cavity with, conformably taking the shape of the mold [Figure 1(e)]. The wavelength of the nanowires after shaping is as small as 80 nm. When the mold cavities have high aspect ratio and sharp edges (no fillet), instant fracture of the NW occurs due to local concentration of severe plastic deformation [Figure 1(h)]. The strain concentration is caused by both shearing and tension. As a result, the NW breaks into shorter segments, with the new length defined by the dimension of the mold cavities [Figure 1(i)]. The advantage of this cutting method is that a large amount of NWs can be cut at the same time in one step operation, which is superior to other NW cutting method, such as electrical beam cutting. The third type is bending of NWs, which is obtained by using an elastomeric polymer mold [Figure 1(f)]. Due to the high elasticity of the polymer material, the mold is bended by the shock pressure during the forming process. Accordingly, the NW deforms with the bended surface of the polymer mold, resulting in bending [Figure 1(g)]. In addition, with the elastomeric material play the role of "cushion" layer which absorbs the shock energy, the deformation is uniform along the bended NWs compared to conformal shaped ones. If there is no cavity on the substrate but only a flat surface, lateral compression of the NWs can be obtained [Figure 1(j)].

Detailed analysis on conformal shaping of silver NWs are given in Figure 2. The NWs can be formed into either periodic or aperiodic wavy structure. Figure 2(a) shows a SEM image of a NW with half shaped into quasi-rectangular waves, and AFM is used to measure the height profile along the deformed NW, as shown in Figure 2(b). It can be seen that the shape of the mold is well taken by the NWs, with the feature size as small as 80 nm and depth of 60nm. However, with a rigid mold used for good shape copy in conformal shaping process, the compression effect of the shock pressure on the part of NW located at the bar position of the mold is significant, preventing the NWs to be formed into high aspect ratio features, as illustrated in Figure 2(c-d). The compression effect is especially severe when high laser intensity is used. Applying elastomeric material layer on top of NWs effectively reduces the compression effect. As shown in Figure 3(e), a layer of 10 nm PVP coating increases the laser shock pressure by 100 MPa to compress a silver NW to the same compressive strain, and a layer of 1 µm PVA coating increases 400 MPa. By further adopting polymer mold, the compression effect can be almost eliminated, which becomes a bending process. There is no obvious compression observed in bended NW, and the NWs are uniformly elongated in bending process.

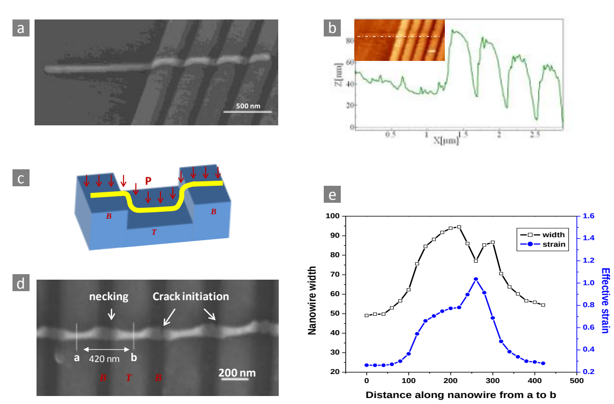

Figure 2 Conformal shaping of NWs.

The silver NWs also exhibited superplasticity during the high strain rate forming process. A NW deformed to its forming limit in conformal shaping is shown in Figure 2(d). Fracture takes place when the deformation exceeds the forming limit of the NW. The formed shape of NWs preserves after crack initiation. Necking takes place before crack initiation, indicating a ductile fracture type of silver NWs, which is in consistent with bulk silver. For unit feature in the periodic wavy NWs, the elongation can be estimated. It is assumed that the NW is pinned at the bar center position of the mold by the strong shock pressure, so the maximum elongation is estimated as 30% for conformal shaping. The classic equation $\varepsilon_l = \ln(\frac{l_d}{l_0}) = \ln(\frac{A_0}{A_d})$ can be used to calculate the tensile strain, and the effective strain is calculated from the von Mises criteria $\varepsilon_{eff} = \sqrt{\frac{2}{3}\left(\varepsilon_1^{\ 2} + \varepsilon_2^{\ 2} + \varepsilon_3^{\ 2}\right)}$. The width variation and corresponding effective strain from point ***a*** to ***b*** in Figure 2(d) are measured, calculated and plotted in Figure 2(e). It can be seen that the width level of the NW in bar region (B) and trench region (T) are different, which is caused by compression effect of the pressure on bar region. The effective strain has the same trend, which is much higher at the bar region, suggesting obvious contribution of compression in the effective strain, which lowers the elongation limit of the NWs. Thus, reducing compression effect will yield more uniform deformation distribution and increases the attainable feature aspect ratio. A dent is observed on the width variation curve, which corresponds to the necking position on the NW. The local effective strain at the necking position suddenly increases to as high as 1.05, indicating a very good ductility of the silver NWs.

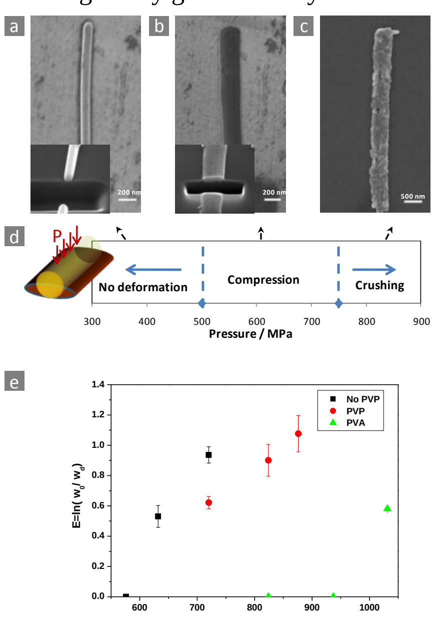

Figure 3 Lateral compression of NWs.

The results on lateral compression of NWs are shown in Figure 3. Figure 3(a) and (b) show the SEM images of a NW before and after laser pressure compression. The inlets show the corresponding cross sections cut by FIB, and the samples are tilted 52 degree. It can be seen that the wire sustained a dramatic shape change from a round cross section to a flat ribbon shape, and the compressive strain is high (~0.85). The relationship between laser shock pressure and compressive strain was calibrated. The plastic compression starts at about 500 MPa, which is about 10 times larger than the yield strength of bulk silver. It is in consistent with the increasing yield strength with the decreasing size. The main reason is that the internal defect becomes less and less with the decreasing size. And a sufficient energy is needed to activate and nucleate dislocations. When the shock pressure exceeds 500 MPa, NWs start to be compressed, and the compressive strain is increasing with the pressure until about 750 MPa. When the shock pressure is higher than 750 MPa, crushing of the nanowires is observed. As seen in Figure 3(c), the NW is crushed into a collection of nano pieces. The ultimate compressive strain obtained without sign of crushing is estimated to be ~ 1.1, and thus the effective strain is nearly 1.4. Therefore, the silver NW shows very good ductility in both bending and lateral compression.

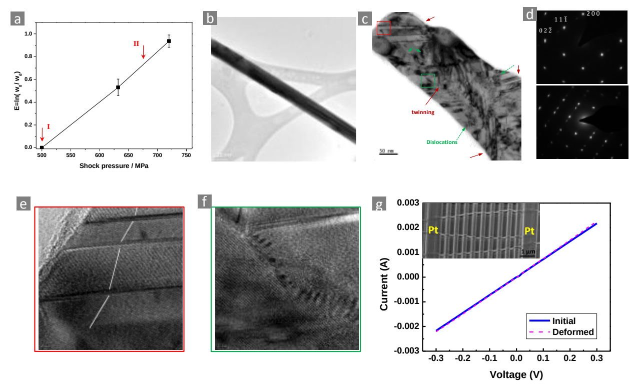

Figure 4 Microstructure characterization and electrical property measurement of deformed Ag NW.

Plastic deformation is always accompanied by the change of microstructure in the material, due to dislocation motion and multiplication. Here, the microstructure evolution of the silver NW laterally compressed by shock pressure is directly observed by TEM, as seen in Figure 4(b-f). Figure 4(b) shows the TEM image of an original Ag NW. When the pressure is less than 500 MPa, as indicated by red arrow in Figure 4(a), no deformation is induced in the Ag NWs. Figure 4(c) shows the TEM image of a NW deformed by a high pressure of 680 MPa, marked as position II in Figure 4(a), and the corresponding compressive strain is almost 0.8. Both are observed from the zone axis [110]. The corresponding selected area diffraction patterns (SADP) are shown in Figure 4(d). It can be seen that the as-received silver NW is quite uniform and defect free with a single

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crystal structure. After compression, high density of deformation twins were observed in NWs. Meanwhile, pile ups of dislocations also appear in the inner part of the NW. Figure 4(e-f) shows high resolution TEM images of certain areas of the deformed NW. Different from plastically deformed bulk material, the dislocation density in the NWs is relatively low. It was observed that the main deformation mechanism of silver NWs under dynamic shock loading is controlled by twinning and stacking faults formation. The dense deformation twins start from the surface of the NW and goes into the inter part, indicating that the partial dislocation first nucleates at the surface and slips afterwards. The reason for surface to be the favorable nucleation position is the lack of defect in NWs due to their small radial dimension. The boundaries of severely deformed NWs are no longer straight and uniform, which is caused by formation of partial dislocations. The formation of closed spaced deformation twins explains the good ductility of the Ag NWs, as the twin boundaries can be available as dislocation sources with further straining.

Two reasons are responsible for the observed deformation twins in the compressed Ag NWs. The first one is small grain size. For bulk FCC metal, the critical twinning stress is much higher than the slip stress. The critical grain size can be estimated by [21]

$$D_c = \frac{2\alpha\mu(b_N - b_p)b_p}{\gamma} \quad (1)$$

where μ is shear modulus (~30 GPa for silver), γ is the stacking fault energy [~23 mJ/m^2 for silver], α reflects the character of the dislocation, b_N and b_P are the magnitudes of the Burgers vectors of the perfect dislocation and the Shockley partial dislocation, respectively. Taking α=1, the estimated D_c is about 60 nm for silver. However, the size of silver NW used in the experiment (~100 nm) is quite large compare to the estimated critical size for twinning to be dominant. Thus, besides small size, there is another important reason for twinning and stacking faults formation in the lateral compressed NW, which is the ultra high strain rate generated by laser shock pressure. The dislocation-slip process is suppressed when the strain rate is high, assisting the formation of deformation twins.

The electrical conductivity of the Ag NW before and after laser forming was also studied. Two terminal electrical measurements were made, as shown in the figure 4(g). The shock pressure applied to deform the NW is about 680 MPa, given as position II in Figure 4(a). It can be seen that the two resultant I-V curves are almost identical, with obvious linearity and a stable ohmic resistance of 137 Ω for the original Ag NWs and 135 Ω for the deformed Ag NWs. The negligible change in the I-V curve indicates that the severe plastic deformation induced by laser forming does not diminish the good conductivity of Ag NW.

In a summary, laser shock based technique for controlled forming of nanowires provides a potential pathway for massive forming and machining of metallic nanowires, and it has the following advantages: 1) the process provides a unique scalable nanomanufacturing for NWs at room temperature, atmospheric pressure, with no vacuum system and no lithography; 2) one step fast process – the duration of laser pulse is only tens of nanosecond; 3) tunable – the shape/size of the nanowires could be manipulated by the laser and mold conditions; 4) flexible – it has been used to deform nanowires of various materials.

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