Silicon doping induced bending in aluminum nanowires

Hung-Jen Chen, Yen-Yu Chen, Chin-Hua Hsieh, Su-Jien Lin, Li-Jen Chou, and Wen-Kuang Hsu

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

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Bent aluminum nanowires are produced by heating equimolar mixture of aluminum and silicon, and bending is due to Al–Si formation. Calculation reveals that incorporation of Si into metal lattice induces cell stress, leading to nanowire growth deviation. An energy barrier is established at nanowire bends, similar to junction devices. © 2007 American Institute of Physics. [DOI: 10.1063/1.2430780]

The conversion of planar structure into curve topologies via defects has been previously demonstrated by fullerene related molecules, for example, 12 pentagonal rings change graphene sheets into rounded molecules and carbon nanotubes become bent when a pair of pentagon and heptagon are deposited at opposite sides of the tube; meanwhile, local density of states also varies significantly at defective regions. In this work, bent aluminum nanowires are produced and Al–Si domains are detected at knee region. Calculation reveals that introduction of smaller Si atoms into Al lattice induces stress, which diverts the growth direction of nanowires. The doping also varies the density of states (DOS) pattern near to Fermi level ($E_F$) and energy bands slightly downshift to negative region.

Equimolar mixture of fine Al and Si powders (400 mesh, 99.9% purity, Aldrich) loaded on an alumina container was heated in a ceramic tube in the presence of a 100 SCCM (SCCM denotes cubic centimeter per minute at STP) Ar/H$_2$ flow (9:1). The furnace temperature was raised to 900 °C for 1 h and the sample was then allowed to cool to room temperature. This procedure generates bent nanowires directly on powder surfaces [arrows, Figs. 1(a)–1(g)] and bending angle varies from wire to wire (60°–180°). Figure 2(a) shows high-resolution transmission electron microscope (HRTEM) image of a selected nanowire bent by approximately 70° and lattice fringes are well defined. Selective area energy dispersive x-ray analysis (EDX) carried out on regions marked as A–D shows only Al signal (see supporting information, S1), and additional peak seen at bending region H corresponds to Si (S1); no Si is detected at regions E–G. 20 bent nanowires have been examined and Al–Si phase is always detected at knee region; the average Si content is 5–7 at.%. Diffraction analyses by fast Fourier transformation (Digital-Micrograph, Gatan) have been carried out to identify crystal structures along wire axis (S2 and S3) and the corresponding delineation is shown in Fig. 2(b). Two types of crystal planes are present vertical to wire axis, i.e., the (200) and (111); the former appears at regions A–C and the latter for region D. On the other hand, the bending area consists of multiple domains, including twin (111) for region E, (111) for region F, (111) for region G, and (200) for triangular H. Although bent nanowires contain various domains but only two zone axes have been identified, i.e., the zone axis of regions A–C is (023), and (011) for regions D–H (S2 and S3). This means that domains D–G are cozonal of (111), and structural transitions have occurred between regions D and C, between regions C and G, and between regions B and E [Fig. 2(b)]. Polycrystalline structures suggest that nanowire growth is unlikely to be vapor-liquid-solid (VLS), but solid-liquid-solid mechanism. Firstly, the VLS mostly leads to single crystal structure. Secondly, the starting materials are equimolar mixture of Al and Si, so both elemental concentrations should be stoichiometrically identical at nucleation sites; in other words, Si should have appeared elsewhere than at knee position. Thirdly, the Al–Si alloy is a solid solution system and Si-eutectic point is 12.16 at.% at 577 °C. Our experimental conditions were set at two-phase region where the stable phases are liquid Al and solid Si; therefore, the Si is dissolved into liquid Al between 660 and 900 °C until the eutectic point is reached (S4). This produces Al-enriched phase and Al–Si domains emerge as a result of eutectic precipitation, as consistent with alloy domain found in nanowires.

 Nanowire bending implies the deviation of crystal growth direction, possibly due to Al–Si domain formation.

![Image](https://via.placeholder.com/150)

**FIG. 1.** Low magnification scanning electron microscopy (SEM) images of nanowires grown from Al–Si particles (a) and enhanced SEM images of bent Al nanowires [(b) and (c)]. Arrows indicate the bends.
Firstly, alloy phase is always detected at knee. Secondly, it is unlikely that growth deviation occurs during structural transition, e.g., from regions G–H or from regions E–H, because bending did not take place at other interfacial transitions, e.g., between regions D and C and between regions C and G. Thirdly, as mentioned above alloy domain is produced via eutectic precipitation, which is different from nanowire growth process. The Al–Si precipitation at two-phase region is mainly determined by surface energy of grain boundary rather than interface energy, and particles often contain large strain energy. Here we believe that alloy formation diverts the nanowire growth and the underlying mechanism involves cell stress induced by Si doping. The cell stress of Si doped Al lattice and the cell pressure is 1/3 of the stress tensor; note that diagonal elements of stress tensor have been modified in order to keep anisotropic term unchanged. Negative values of external stress and pressure indicate that doped structure undergoes a stretching-type strain and the corresponding cell stress is 2.57 GPa. This outcome gives a reasonable explanation for nanowire bending, because incorporation of a stressed crystal domain into a growing nanowire leads to deviation and the structure can be bent in two fashions. Firstly, if alloy domain is embedded at the right side of nanowire, the stress forces regions E and G normal to 111 planes toward left, resulting in left bending. Secondly, nanowire becomes right bending if stressed domain is deposited at the opposite side. The twin structure domain E adjacent to knee is noteworthy because similar structures are frequently seen in bent nanowires. Twin defects often emerge at 111 planes during Al–Si solidification, which is attributed to lower interface energy than surface energy of grain boundary. As a result, anisotropic growth prevails and self-perpetuating steps appear at growing front, leading to twin-plane reentrant edge mechanism. In our study, twin defects may act as buffer layers for releasing press from alloy domain. Firstly, domains H and E have the same zone axis (011), so lattice translation from H (200) to E (111) planes (vice versa) can be simply achieved via screw dislocation, accompanied by spacing changes from 4.05 to 4.03 Å.

\[ \begin{array}{ccc}
 x & y & z \\
 2.57 & 0 & 0 \\
 0 & 2.57 & 0 \\
 0 & 0 & 2.57 \\
\end{array} \]

**TABLE I.** Al cell stress induced by Si doping. \( xx, yy, \) and \( zz \) represent the target tensile stress and \( yz, xz, \) and \( xy \) for the target shear stress (\( P = -2.57 \text{ GPa} \)).

![FIG. 2. HRTEM image of selected bent nanowire (a) and corresponding structures along wire axis (b).](image)

![FIG. 3. (Color online) Calculated Si doped Al cell; yellow for Si atoms and pink for metal atoms (a), simulated Al crystal structures of 200 plane (left) and 111 planes (right) (b), and delineation of crystal structures at interface between regions E and H (c).](image)
and the nearest Al atoms become positive while far atoms maintain negative, for example, the nearest and second Al atoms are 0.01 and −0.02 respectively, relative to Si (−0.08) [Fig. 3(a)]. The electronic structures shown here is interesting because typical semiconductor devices (e.g., $p$–$n$ junctions) usually use Si as matrix and III or V elements as dopants. Here matrix material is Al and small content of Si doping has depressed the band [sum curve, Fig. 4(a)] by 0.15 eV, which means that an energy barrier is established at knee region. The built-in potential for bent carbon nanotubes is 0.1 eV, which generates an obvious Schottky effect. Here bent nanowires possess slightly higher potential barrier at knee and similar effect may be anticipated.

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