Phase-equilibrium-dominated vapor-liquid-solid mechanism: further evidence

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ABSTRACT Prediction and design of various nanomaterials is a long-term dream in nanoscience and nanotechnology, which depends on the deep understanding on the growth mechanism. Herein, we report the successful prediction on the growth of AlN nanowires by nitriding $\text{Al}_{69}\text{Ni}_{31}$ alloy particles across the liquid-solid (β) phase region (1133–1638°C) based on the phase-equilibrium-dominated vapor-liquid-solid (PED-VLS) mechanism proposed in our previous study. All predictions about the growth of AlN nanowires, the evolutions of lattice parameters and geometries of the coexisting Al-Ni alloy phases are experimentally confirmed quantitatively. The preconditions for the applicability of the PED-VLS mechanism are also clarified. This progress provides the further evidence for the validity of the PED-VLS mechanism and demonstrates a practical guidance for designing and synthesizing different nanomaterials according to corresponding phase diagrams based on the insight into the growth mechanism.

Keywords nanowires growth; prediction; growth mechanism; phase equilibrium; quantitative experimental analysis

INTRODUCTION

Nanomaterial synthesis is experiencing a profound evolution from the empirical science (“cook-and-look”) to prediction and design which depends on the deep insight into the growth mechanism [1–3]. A typical empirical synthesis is the growth of various one-dimensional (1D) nanomaterials by the classical vapor-liquid-solid (VLS) process, which was first proposed in 1964 [4] and is the most popular method today [5–8]. Due to its great success and significance, persistent effort has been devoted to exploring the origin of the VLS process over the past half-century. Especially, by applying the advanced *in situ* microscopic technique, the real-time nucleation and growth process of individual nanowires has been directly observed and the involved kinetics is studied thoroughly [9–16]. Despite such kind of progresses, the precise prediction on nanomaterial synthesis is still a great challenge. Based on the quantitative experimental analysis, recently we proposed the phase-equilibrium-dominated VLS (PED-VLS)

mechanism for the growth of h-AlN nanowires by nitriding $\text{Al}_{69}\text{Ni}_{31}$ particles in the liquid-solid (δ) phase region (854–1133°C) [17]. Specifically, at a certain temperature, the yield of AlN nanowires and the composition of the residual Al-Ni alloy are determined by the Al-Ni binary phase diagram. This specific example reveals the possibility to predict and design nanomaterials according to the corresponding phase diagrams. Herein we report the successful prediction of the growth of AlN nanowires by nitriding $\text{Al}_{69}\text{Ni}_{31}$ alloy particles across another liquid-solid (β) phase region (1133–1638°C). By using the rapid quenching and growth tracing approaches, all expectations about the growth of the AlN nanowires, the evolutions of lattice parameters and geometries of the coexisting Al-Ni alloy phases were experimentally confirmed quantitatively. The preconditions for the applicability of the PED-VLS mechanism were also clarified. This study provides the further evidence for the PED-VLS growth mechanism, and also corroborates its validity in designing 1D nanostructures.

EXPERIMENTAL SECTION

Nitriding $\text{Al}_{69}\text{Ni}_{31}$ alloy particles and quenching the products

Nitridation of $\text{Al}_{69}\text{Ni}_{31}$ alloy particles is similar to that in our previous study [17] but in different temperature range, i.e., in the region II of Fig. 1a. The $\text{Al}_{69}\text{Ni}_{31}$ particles were dispersed on an alumina plate, and then mounted at the center of a tube furnace (Supplementary information, Fig. S1). The $\text{Al}_{69}\text{Ni}_{31}$ alloy particles consist of two phases of o- Al_3Ni and h- Al_3Ni_2 (Fig. S2) with size distribution in the range of 1–100 μm [17]. After being pumped and flushed by Ar for several times to remove oxygen and moisture, the furnace was heated up to a desired temperature under N_2 flow of 100 mL min^{-1} . After 2 h nitridation, the product was pushed into liquid N_2 cooling zone for rapid quenching to avoid phase separation. For comparison, the products were also obtained by slow cooling, i.e., naturally-cooling

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to ambient temperature in the furnace, and in this case the phase separation might occur.

Tracing the growth of AlN nanowires out of a specific particle

$\text{Al}_{69}\text{Ni}_{31}$ particles were scattered on an alumina wafer. The growth of AlN nanowires out of an identified Al-Ni particle was traced by scanning electron microscopy (SEM). Specifically, the identified Al-Ni particle was first nitrided slightly below the phase transition temperature of 1133°C and SEM image was recorded. Then, the same particle was further nitrided slightly above 1133°C and SEM image was obtained again. Thus the morphological evolution was traced.

Monitoring the heat flow and weight change during nitridation

Nitridation process was monitored *in situ* by thermogravimetry-differential scanning calorimetry (TG-DSC, STA-449F3 thermal analyzer, Netzsch) from room temperature to 1400°C at a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 . The control experiment was performed by keeping additional 1 h at 1050°C during nitridation. The survey in Ar was also conducted for comparison.

Sample characterizations

The products were characterized by SEM (Hitachi S-4800), high resolution transmission electron microscopy (HR-TEM, JEM-2100) attached with an energy dispersive X-ray spectroscopy (EDS) detector, and also precisely identified by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer, Cu $\text{K}\alpha$, scan speed: 0.15 s per step, step size: 0.019757).

RESULTS AND DISCUSSION

In preparing AlN nanowires, the source $\text{Al}_{69}\text{Ni}_{31}$ particles consist of two phases of o- Al_3Ni and h- Al_3Ni_2 (Supplementary information, SI 1). As well known, in the liquid-solid (δ) two-phase region I (854 – 1133°C) (Fig. 1a), the $\text{Al}_{69}\text{Ni}_{31}$ particles experience a PED-VLS growth to form h-AlN nanowires and coexisting solid solution of δ phase (denoted by h- Al_3Ni_2). The composition of the δ phase changes along the solidus cd with increasing the nitridation temperature. And the measured weight gain due to the formation of h-AlN nanowires is in quantitative agreement with the theoretical calculation according to the PED-VLS mechanism [17].

Based on the PED-VLS mechanism, we predict the growth of AlN nanowires in the liquid-solid (β) two-phase

Figure 1 Predicting and tracing the second-stage growth of h-AlN nanowires. (a) Al-Ni phase diagram (data from [18]). The dashed line highlights the composition of the $\text{Al}_{69}\text{Ni}_{31}$ alloy. (b) Prediction on the second-stage growth of h-AlN nanowires by increasing the nitridation temperature across the phase transition from region I into II in (a) at 1133°C based on the PED-VLS mechanism. The schematic second-stage growth is also shown in the inset in (a). (c and d) SEM images of an identified $\text{Al}_{69}\text{Ni}_{31}$ alloy particle after nitridation at 1100°C for 2 h (c), followed by additional 2 h nitridation at 1200°C (d).

region II (1133–1638°C), as schematically shown in Figs 1a and β . First, with further increasing the nitridation temperature across 1133°C from region I into region II, the new liquid Al-Ni phase and solid β phase (c-AlNi) will appear at the expense of the δ solid (h-Al₃Ni₂) due to its incongruent melting. This means that some additional Al species will be ‘unfrozen’ during this transition and interact with nitrogen to form AlN. Accordingly, a second-stage growth of AlN nanowires will occur following the first-stage growth in phase region I, accompanied by forming additional β phase while keeping the geometry approximately unchanged. Second, the composition of the β phase should change along the solidus *ef* (Fig. 1a) with increasing the nitridation temperature. Third, the amount of AlN nanowires formed at a specific temperature, which can be experimentally measured, should also be in quantitative agreement with that predicted by the PED-VLS mechanism. These three predictions are indeed experimentally confirmed as following.

First, the second-stage growth of AlN nanowires is evidenced by tracing the growth on an identified Al₆₉Ni₃₁ alloy particle as shown in Figs 1c and d. The particle was completely nitrided at 1100°C in region I for 2 h, and SEM reveals many AlN nanowires growing out of the particle (Fig. 1c). Then, the same particle was nitrided at 1200°C in region II for additional 2 h (Fig. 1d). By comparing Figs 1c and d, we find that the nanowires in Fig. 1c become longer in Fig. 1d and some new nanowires appear, while the coexisting Al-Ni bulk almost maintains its geometry (Fig. S3). The growth of AlN nanowires out of the coexisting Al-Ni bulk was confirmed by SEM, TEM and EDS characterizations on the products obtained at different nitridation temperatures (Fig. 2). Generally more AlN nanowires grow out of the Al-Ni alloy particles at higher nitridation temperature (Fig. 2a). The traced second-stage growth of AlN nanowires results from the emerging Al-Ni liquid phase due to the phase transition, i.e., the incongruent melting of the δ solid, by increasing the nitridation temperature across 1133°C, as expected from the PED-VLS mechanism (Figs 1a and b). The second-stage growth of AlN nanowires and their increasing tendency with nitridation temperature are also confirmed by *in situ* TG-DSC examination discussed later. Notably, the growth of AlN nanowires here follows the VLS mechanism, different from the dislocation-driven growth of AlN nanohelices [19] and nanowires [20].

Second, the evolution of the products with different nitridation temperature in region II is characterized by XRD. The high-resolution spectra and derived results are presented in Fig. 3. The product is composed of h-AlN and c-AlNi (β) (Fig. S4), which is different from that consisting

of h-AlN and h-Al₃Ni₂ (δ) formed in the first-stage growth in region I [17]. The disappearance of h-Al₃Ni₂ (δ) and the appearance of c-AlNi (β) are in agreement with the anticipation of the PED-VLS mechanism (Figs 1a and b). We observed that the rapid-quenching technique is required to keep the state after the nitridation, otherwise phase separation of the solid c-AlNi (β) might occur during the slow cooling, leading to the appearance of h-Al₃Ni₂ (SI 3). Generally, the relative intensity of the diffraction peaks for h-AlN shows an increasing tendency with elevating the nitridation temperature as expected (Fig. S4), in accordance with the intuitive SEM observation on the evolution of the nitridation products (Fig. 2a). Furthermore, from the local enlargement of the XRD patterns, it is clearly seen that the three characteristic peaks of (100), (002), and (101) for h-AlN have negligible shift (Fig. 3a). In contrast, the three characteristic peaks of (100), (110), and (211) for c-AlNi show progressive shifting toward the lower angles as increasing reaction temperature, with better resolution at the higher angle side in the order of group (100) < (110) < (211) (Figs 3b and SI 4), arising from the increasing lattice parameter *a* (Fig. 3c). The temperature dependence of the lattice parameter *a* is re-plotted as the corresponding composition dependence by referring to the phase diagrams [18,21], and presented as the red and blue curves in Fig. 3d. Surprisingly, the changing behavior is in quantitative agreement with that for Al-Ni alloy along solidus *ef* (Ni content: 42–50 at.%) [22,23], with a systematic error of Ni content of ca. 2 at.% (or lattice parameter of ca. 0.007 Å) in reference to the updated data of 1972 [23] (Figs 3d and SI 5). This result proves that the composition of the β phase in the product indeed changes along the solidus *ef* with increasing the nitridation temperature.

Third, the nitridation process of the Al₆₉Ni₃₁ particles has been *in situ* examined by TG-DSC in a wide temperature range up to 1400°C, as depicted in Fig. 4. Briefly, the two endothermic peaks at ca. 859 and 1133°C in the DSC curves (either in Ar or in N₂ flow) come from the respective phase transitions (Fig. 1a), and the additional broad exothermic peak in N₂ centered at 938.4°C comes from the nitridation of the Al-Ni particles. The TG curve in inert Ar is featureless, while that in N₂ presents an increasing tendency following the first phase transition due to the growth of AlN nanowires. It is worth noting that an upward step appears in the TG curve following the second phase transition (Fig. 4a), also reflected by the peak starting at 1134.2°C in the corresponding differential TG (DTG) curve (Fig. S6a). This phenomenon is in agreement with the observed second-stage growth of AlN nanowires on the identified Al₆₉Ni₃₁ alloy particle (Figs 1c and d). Such

Figure 2 SEM, TEM and EDS characterizations. (a) Typical SEM images of the products obtained at 1200, 1300 and 1400°C. (b) TEM image of the AlN nanowires. (c) HRTEM image of a typical nanowire in (b) marked by the white arrow. Inset is the corresponding fast Fourier transform (FFT) pattern. The interplanar spacings of 2.72 and 2.51 Å correspond to the $d_{(100)}$ and $d_{(002)}$ values for h-AlN. (d) EDS spectra taken from the nanowires (site 1) and bulk (site 2). The nanowires consist of Al and N elements, and the coexisting bulk consists of Al and Ni elements. C and Cu signals come from the TEM grid.

phenomenon is even more obvious by keeping additional 1 h at 1050°C for full nitridation and then further raising it across the second phase transition (SI 7). Thanks to the sufficient nitridation time, in this case the liquid Al-Ni phase formed below 1050°C is completely consumed for forming AlN nanowires. With the less interference of the hysteretic nitridation reaction, the weight gain from the second-stage growth following the second phase transition is more prominent, and the corresponding DTG signal also becomes much stronger (Fig. S7a).

Moreover, the weight gain read from the TG curve quantitatively coincides with the theoretical calculation

based on the PED-VLS mechanism in the whole temperature range (Figs 4c and SI 8). Specifically, the experimental and theoretical weight gains exhibit a quite similar increasing tendency vs. temperature even in the detail of the upward step for the second-stage growth of AlN nanowires following the phase transition at 1133°C. Generally, the experimental value is a bit smaller than the theoretical value, and the deviation between them is getting smaller with increasing the nitridation temperature and approaching zero at 1400°C. Such deviation comes from the hysteretic nitridation of the liquid Al-Ni phase due to the kinetic limitation in the continuous temperature-rising manner,

Figure 3 Quantitative XRD characterization of the nitridation products. (a) The (100), (002), and (101) peaks of h-AlN with negligible peak shift for the products with different nitridation temperatures. (b) The (100), (110), and (211) peaks of c-AlNi (β) showing the progressive down-shifting with increasing the nitridation temperature. (c) Lattice parameters a and c of the h-AlN (black) and lattice parameter a of the c-AlNi (red) vs. growth temperature (SI 4). (d) Composition dependence of the lattice parameter a of the c-AlNi. The data are converted from the corresponding temperature dependence in (c) by referring to the experimental [18] (red: $\square$ —) and calculated [21] (blue: $\square$ —) phase diagram, respectively. For comparison, two reported relationships of the lattice parameter vs. composition of β phase (c-AlNi) along solidus ef are also listed in (d) (black: $\blacktriangle$ —; $\triangle$ —. Data from [22,23]).

especially at low temperature side for the low reaction rate. This argument is confirmed in our control experiment by fully nitriding the alloy at 1050°C for additional 1 h, which leads to a continuous increase of the weight gain from the initial 6.2% to 7.7% of ca. 40 min later, and then keeping unchanged in the following 20 min (Expt.^b: * in Figs 4c and S7a). The weight gain of 7.7% at 1050°C is indeed very close to the theoretical values (Theor.^c: $\blacksquare$ — and Theor.^d: $\square$ — in Fig. 4c) predicted by the PED-VLS mechanism. The less obvious upward step in the experimental curve than those in the two theoretical curves also results from the hysteretic nitridation. Therefore, the experimentally measured weight gain due to the growth of AlN nanowires is in quantitative agreement with the prediction of the PED-VLS mechanism.

The preceding experimental results clearly indicate that all the predictions on the second-stage growth of AlN nanowires by nitriding $\text{Al}_{69}\text{Ni}_{31}$ particles in the liquid-solid (β) phase region of 1133–1638°C (Figs 1a and b) are proved not only qualitatively but also quantitatively. The successful predictions provide the further evidence for the validity of the PED-VLS growth mechanism in designing 1D nanostructures.

However, it should be pointed out that in some cases the PED-VLS mechanism is not applicable. For instance, in the efforts to prepare ZnO nanowires by oxidizing $\text{Cu}_{66}\text{Zn}_{34}$ alloy [24] and In_2S_3 nanowires by sulfurizing $\text{Cu}_{11}\text{In}_9$ alloy [25], the predictions of the PED-VLS mechanism are ineffective. For the former, the growth happened as the $\text{Cu}_{66}\text{Zn}_{34}$ alloy still existed in the solid single-phase region, i.e., before entering the liquid-solid two-phase region. For the latter, though the $\text{Cu}_{11}\text{In}_9$ alloy was in the liquid-solid two-phase region, both phases reacted with the introduced gaseous H_2S , thus CuInS_2 film rather than 1D In_2S_3 nanowires was formed. In principle, for binary alloys, the PED-VLS mechanism works only when the liquid phase in the liquid-solid two-phase region (e.g., the liquid Al-Ni in regions I or II in Fig. 1a) can selectively react with the introduced gaseous reactant (e.g., N_2 in this study). In other words, the appearance of the liquid-solid two-phase coexistence and the selective reaction of the introduced gaseous reactant with the liquid phase are two preconditions when applying the PED-VLS mechanism for the prediction and design of 1D nanomaterials.

Attention should also be paid to optimizing the experimental condition, e.g., by prolonging reaction time, to min-

Figure 4 Thermal analysis on the $\text{Al}_{69}\text{Ni}_{31}$ alloy particles in N_2 or Ar flow with the heating rate of $10^\circ\text{C min}^{-1}$. (a) TG-DSC curves in N_2 . (b) TG-DSC curves in Ar. (c) Theoretical and experimental weight gains vs. temperature in N_2 . Expt.^a (—●—): a replotted of TG curve in (a). Expt.^b (*): the weight gains at beginning (6.2%) and 40 min later (7.7%) during the temperature-keeping control experiment at 1050°C (Fig. S7a). The arrow indicates the increasing trend with time prolonging. Theor.^c (—■—) and Theor.^d (—□—): theoretical calculations with reference to the experimental [18] and calculated [21] phase diagrams, respectively (SI 8).

imize the influence of kinetic limitation as reflected in our TG-DSC control experiment (Figs 4c and S7). In contrast, by controlling or utilizing the kinetic process, it can provide a non-equilibrium alternative to create some unique nanostructures, as demonstrated in the updated progress in the Al-Si catalyzed growth of the Al-doped Si nanowires with Al content far beyond the equilibrium range [26]. These two complementary approaches are actually becoming the most powerful methods in the design and creation of various nanostructures today.

CONCLUSIONS

We demonstrated the successful prediction for the growth

of AlN nanowires for the first time by nitriding $\text{Al}_{69}\text{Ni}_{31}$ particles across the liquid-solid (β) phase region (1133 – 1638°C), which based on the PED-VLS mechanism. All the related predictions on the evolutions of the nanowires and coexisting bulk alloys were experimentally confirmed quantitatively. The predictions further corroborate the validity of the PED-VLS mechanism. The applicability of the mechanism has also been specified by two preconditions, i.e., the appearance of liquid-solid two-phase coexistence and the selective reaction of the introduced gaseous reactant with the liquid phase. This progress demonstrates a transformation from the empirical science in nanomaterial synthesis into the prediction and design based on the deep insight into the growth mechanism, which is significant for controllable synthesis, functionalization and applications.

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Author contributions Hu Z and Wu Q conceived and supervised the project; Zhang Y, Wu Q, Wang X and Hu Z designed the experiments; Zhang Y, Cai J, Wu Q and Wang X carried out the experiments; Hu Z, Wu Q, Zhang Y, Cai J, Yang L, He C and Wang X analysed the data and prepared the manuscript. Hu Z and Wu Q are co-corresponding authors of this manuscript. All the authors participated in discussions of the research.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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相平衡主导的气-液-固生长机理: 进一步的证据

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摘要 纳米材料的预测和设计是纳米科学与技术领域的长期梦想, 该梦想的实现有赖于对生长机理的深刻理解. 本文基于我们前期研究揭示的相平衡主导的气-液-固(VLS)生长机理, 成功地预测了在1133~1638°C温区内通过氮化 $\text{Al}_{65}\text{Ni}_{35}$ 合金颗粒生长AlN纳米线的过程, 有关AlN纳米线的生长、共存Al-Ni合金相的晶格参数及形貌演变等预测均得到了定量化实验结果的证实, 并界定了相平衡主导的VLS生长机理的适用条件. 本文为相平衡主导的VLS生长机理的有效性提供了进一步的实验证据, 同时展示了在生长机理的指导下根据相图设计和制备纳米材料的一个实例.