Four-dimensional Probing of Phase Reaction Dynamics in Au/GaAs Nanowires

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ABSTRACT: Nano-eutectic phase reaction covers the fundamental study of a chemical/physical reaction of multiple phases at the nanoscale. Here we report the direct visualization of phase reaction dynamics in Au/GaAs nanowires (NWs) using four-dimensional (4D) electron microscopy. The NW phase reactions were initiated with a pump laser pulse while the following dynamics in the Au/GaAs NW was probed by a precisely time-delayed electron pulse. Single-pulse imaging reveals that the cubic zinc-blende NW presents a transient length increase within the time duration of ~ 150 ns, giving the appearance of intermediate phase reactions at an early stage. A final length reduction of the NW is observed after the phase reactions have fully ended. In contrast, only length reduction is seen throughout the entire process in GaAs/AlGaAs core-shell and hexagonal wurtzite GaAs NWs. The reasons for the above intriguing phenomena are discussed. The eutectic-related phenomena in both zinc-blende and wurtzite materials offer a comprehensive understanding of phase reaction dynamics in polytypic structures commonly available in compound semiconductors.

KEYWORDS: GaAs nanowires, Phase reactions, Structural dynamics, Ultrafast dynamics, 4D electron microscopy

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The rapid advance of novel nanodevices facilitates the progressive investigation of semiconductor nanostructures, e.g., nanowires (NWs), because of their unique structural, electrical and optical properties [1-6]. Nanostructured compound semiconductor materials (II-VI, III-V and IV-IV group materials) generally exist in more than one structural arrangement, namely, in the forms of polytypes. Polytypism occurs in the same material when the geometry of a repeating structural layer is maintained but the layer stacking sequence of the overall crystal structure varies. Polytypes in compound semiconductor NWs have two common kinds of structures: cubic zinc-blende (ZB) and hexagonal wurtzite (WZ). Different polytypes have been shown to affect the optical, electrical and mechanical properties [7-10]. The synthesis/growth of various polytypic NWs has been amenable to direct studies for many decades. A common NW growth technique is the use of metallic nanoparticles as the catalysts via the vapor-liquid-solid (VLS). In order to better understand the growth mechanisms for tailoring and controlling polytypic NWs, comprehensive investigations of the structural effect on the phase reactions with the involvement of multiple phases are essential.

Gallium arsenide (GaAs) NWs are the ideal examples of polytypic materials for fundamental studies, which are also promising for applications in optoelectronic devices, for example, solar cells, photodetectors and lasers [11-14]. The growth of GaAs NWs is generally catalyzed by gold nanoparticles. The Au/GaAs interfacial region is important for realizing the phase reactions, nucleation and successive growth of the NWs. Therefore, the Au/GaAs NWs are ideal systems for detailed microscopic exploration of phase reaction dynamics. Understanding the physics governing the phase reaction dynamics is essential for controlling the structure and composition of the involved substances. Nevertheless, less effort has been devoted to the real-time visualization and further control of the phase reaction dynamics in polytypic NWs. In situ microscopic observation of the phase reaction processes in polytypic structures on the ultrafast timescale offers a window for exploring transient transformation so that the causal link between initial and final states could be unraveled. However, this is a challenging task.

With the development of ultrafast characterization techniques, experimental investigations have spanned a huge range of time scales with the highest temporal resolution down to femtosecond or even

attosecond nowadays. 4D electron microscopy (EM), capturing a well-defined image of an object at each given time point in its evolution by short-duration illumination, is capable of directly visualizing the dynamic behavior of the nano-scaled substances with high spatiotemporal resolution [15-30]. We can then “freeze” intermediate states in the polytypic NWs and study the evolution of microstructures as the phase reactions pass through their transition states, presenting a dynamic picture of the reaction processes in real time and space. The outcome would be a detailed exploration of fundamental mechanisms controlling key processes such as phase reactions in NW nucleation and growth, which would help to improve and tailor the functionality of NW-based devices through microscopically controlling the material structure and composition.

In this letter, we report the direct observation of phase reaction dynamics in the ZB GaAs NWs by 4D EM. The dynamical phase reactions are induced through a temperature jump triggered by an optical laser pulse. We then project sequences of images with precisely delayed photogenerated electron packets, providing the spatiotemporal evolution of phase reaction behavior in the NWs at an early stage. Interestingly, single-pulse imaging shows that with an incoming laser heating pulse the NW length presents a transient increase at the time shorter than ~ 150 ns, and reduces in the final state after the phase reaction process has fully ended. This phenomenon is different from the length shrinkage observed in both the transient and final states of the WZ and the core-shell NWs. The length shrinkage is realized through swallowing the GaAs component by the Au nanoparticle due to the phase reactions between the two components. The phenomena observed in these different structured NWs are compared and the underlying mechanisms are discussed.

GaAs NWs with the ZB and WZ structures were epitaxially grown on GaAs (111)B-oriented substrate by metal-organic chemical vapor deposition. Au nanoparticles were used as catalysts for growing the NWs. To study the coating effect on the phase reaction dynamics, the core-shell NWs (namely, a thin shell layer of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ was coated on the GaAs core) were also grown. The thickness of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (hereafter simplified as AlGaAs) layer is about 20 nm, and the value of x equals to ~ 0.2 [31]. Detailed growth procedures of these NWs are available elsewhere [32, 33]. Besides the role for

catalyzing the NW growth, Au nanoparticles were also employed as the necessary components for studying the eutectic-related phase reactions between Au and GaAs components after the growth.

The morphology of the ZB and core-shell GaAs NWs was investigated by scanning electron microscopy. 4D EM, equipped with femtosecond/nanosecond laser systems, as detailed elsewhere [34, 35], was used to study the phase reaction dynamics of the Au/GaAs composite nanostructures (Figure 1a). The technique is based on the pump-probe scheme. A pump pulse excites the composite material to be studied while a second probe pulse measures the response of the material to the excitation. The technical requirements are synchronization of these two pulses to a well-defined time-axis, permitting reconstruction of the dynamic reaction process undergone. Specifically, femtosecond infrared pulses at a wavelength of 1040 nm (pulse duration of 350 fs) were frequency doubled by second harmonic generation (SHG) to obtain visible laser pulses (520 nm). The generated visible laser pulses were used to initiate the sample dynamics. Nanosecond ultraviolet pulses at 266 nm (pulse duration of 10 ns) were directed to the photocathode to generate electron pulses for probing the dynamics. By varying the time delay between the arrivals of the laser heating pulses (pump) and the electron pulses (probe) at the sample through a digital delay generator, the time evolution of the response can be measured. 4D EM can be operated in either stroboscopic or single-pulse mode. For imaging the irreversible dynamics, single-pulse mode was used. An entire image was formed with only one pulse of $\sim 10^5$ electrons. In the static imaging, stroboscopic mode (repetition rate was 1 kHz) was used because of the high electron counts for better image quality. Details of the procedure are described elsewhere [23, 25].

Figure 1b shows the typical overview of the morphology of the as-grown Au/GaAs NWs on a GaAs substrate. It can be seen that the NWs grew vertically with respect to the GaAs substrate. Each NW is separated by several microns away. Owing to the large separation among the NWs, we could study the phase reaction dynamics from a single NW without the influence of neighboring NWs. In addition, chemical and many physical properties of materials are inherently orientation-dependent, and therefore the similar orientation of the NWs on the substrate allows us to study the statistical properties by selecting many single NWs. The typical microstructures of a ZB GaAs NW and a GaAs/AlGaAs core-shell NW

are presented in Figure 1c. A gold nanoparticle is located at the tip of each NW. These kinds of metal-semiconductor composite nanostructures were used for the following phase reaction studies.

Single-pulse imaging was used to capture the transient features during the eutectic-related phase reactions in the ZB GaAs NWs. The as-grown NWs, which were still intact on the GaAs substrate, were directly loaded into the 4D EM so that any possible ambiguity caused by the supporting films usually present for normal EM samples would be excluded [25]. Furthermore, this kind of sample preparation avoid any damage to the original NWs. Figure 2 shows a typical example of the time-resolved phase reaction dynamics in a ZB NW. The ZB structure of the NW was confirmed by its selected area diffraction pattern. The diameter of the NW was 115 nm. Shown in the first to third columns are single-pulse images of the NW before, at a specific time delay from 20 to 150 ns, and several seconds (phase reaction process ended) after exposure to a single laser pulse (laser fluence of 12 mJ/cm^2), respectively. The time sequences of the pump-probe experiments are schematically illustrated in Figure 2d. The snapshots with the notations of “before” and “end” were taken using the electron pulses under the condition that the laser excitation pulses were blocked, representing the initial and final states of the NW. The image labeling “during” denoted the ongoing dynamics that were probed at a specific time delay with respect to a laser excitation pulse.

When exciting the NW with a laser pulse, we imaged the transient feature of the NW at each specific time delay. The dotted and solid lines marked the initial (before an excitation pulse) and the latter (after an excitation pulse) positions of the NW tips. In all the cases (first and third columns of Figure 2), there were obvious length reductions of the NW after the whole processes had ended (by comparing the initial length of the NW with the final one). Interestingly, however, the NW length showed an intermediate increase of about 45 nm at 20 ns [Figure 2a, second column], compared to that of the initial NW before the laser excitation. When the laser-induced phase reactions had ended, the NW length was shortened by ~65 nm in comparison to the initial length [Figure 2a, third column]. The similar behavior also occurred for the NW taken at 100 ns after the laser pulse excitation [Figure 2b]. The transient increase of the NW length at 100 ns was ~60 nm, which was larger than that at 20 ns. Nevertheless, the NW showed no

obvious increase of the length at 150 ns [Figure 2c, compared to the initial NW length]. It suggests that the transient increase of the NW length was complete in about 150 ns. It should be noted that the diameter of the NW remained relatively unchanged despite the obvious change in length.

The obvious length reduction of the ZB NW in the final states is similar to that observed in the WZ GaAs NWs [25]. The Au nanoparticles would dissociate solid GaAs when the GaAs surface with Au particles is heated. Since arsenic is volatile, it escapes from the system when Ga reacts with Au to form an intermetallic alloy [36, 37]. According to the Au-Ga binary phase diagram [38-40], several intermetallic phases can be obtained at the temperature as low as ~560 K, which is much lower than the melting point of either Au (1337 K) or GaAs (1511 K). Because of these phase reactions between Au and GaAs, the final length reduction of the NW was observed. The vanished part of the GaAs was incorporated into the nanoparticle, resulting in the increase of its size. Single-pulse diffraction was employed to detect the newly formed alloy phases. Similar to that observed in WZ NWs, the phases including Au_7Ga_2 , AuGa and AuGa_2 alloys were found in ZB NWs when excited by laser pulses [25]. However, the effect of ZB and WZ structures on causing the difference of the transient behavior (length increase for the ZB NW while length reduction for the WZ one), will be discussed according to the following experimental results.

Firstly, we investigated the effect of a coating layer on the transient length change of the ZB NWs. This was achieved by growing an additional shell layer of AlGaAs on the ZB GaAs core. Figure 3 shows the phase reaction dynamics in a GaAs/AlGaAs core-shell NW. The first row are the images of the core-shell NW under the excitation of a laser pulse with the threshold fluence of $\sim 25 \text{ mJ/cm}^2$ for the phase reactions [Figure 3a]. Slight morphological changes in the tip region of the core-shell NW were observed between the images with notations “before” and “end”. Using 100 electron pulses for the imaging, the contrasts of such changes were enhanced in the snapshots of the first and fourth columns corresponding to the initial and final states of the core-shell NW, respectively. Note that the threshold fluence for phase reaction to occur in the core-shell NW is at least four times higher than that in the ZB NW. The typical time-resolved micrographs of the phase reactions in the core-shell NW are presented in Figure 3b. Different from the transient length increase observed in the core-only NW [Figure 2], the core-shell NW

shows the reduction of its length at specific time delays (e.g., 20 ns shown in this work) and also at the end of the process. It indicates that the addition of the shell layer may influence the surface diffusion along the NWs, causing this distinct phenomenon from that seen in the core-only NW.

To verify the effect of surface diffusion, we further imaged the phase reactions in the core-only ZB NWs with continuous electron beam so that the electron microscopy micrographs with high contrast can be acquired. Figure 4 shows the fusing behavior of the core-only ZB NW with the laser fluence varying from 5.5 to 25 mJ/cm². The initial state of the NW without the laser irradiation is presented in Figure 4a. After a laser pulse excitation (fluence of 5.5 mJ/cm²), the top part of the NW showed slight morphological change [Figure 4b]. Calculations using a two-temperature model for Au and a three-temperature model for GaAs show that the lattice temperature was around 560 K [25], suggesting that the phase reactions between the Au and GaAs started to occur according to the phase diagram [40]. When the laser fluence was increased to 12 mJ/cm², the lattice temperature was about 900 K [25] and therefore more Au-GaAs components were involved in the phase reactions, causing an increase in the size of the top nanoparticle [Figure 4c]. In addition to the dark feature of the NW tip, additional dark contrast (indicating the existence of the Au element) appeared on the NW, as marked by an arrow. This indicates that the Au species migrated a certain distance away from the nanoparticle and new alloy phases were formed on the NW when the phase reactions were triggered by the laser pulse excitation.

The length of the NW continued to shrink with increasing the laser fluence [Figures 4d-e]. Compared to the NW in Figure 4d, there was a reduction of 375 nm in its length while the diameter of the nanoparticle increased from 175 to 225 nm [Figure 4e]. We estimated the volume change of the NW as well as its tip. The volume reduction of the GaAs NW was $\sim 3.2 \times 10^6 \text{ nm}^3$, which was comparable to the volume increase of the nanoparticle ($\sim 3.1 \times 10^6 \text{ nm}^3$). In all cases, additional dark contrasts (marked by the arrows) were always seen away from the nanoparticle. When the laser fluence was 25 mJ/cm², there was clear fusing of the NW [Figure 4f] at the position where the former dark contrast appeared in Figure 4e. Note that at this fluence the lattice temperature was $\sim 1400 \text{ K}$ from calculations [25], which would not be sufficient to melt the GaAs NW because of its high melting point (1511 K). It indicates that in the presence of Au at

the location with the dark contrast the phase reactions occur with the temperature lower than the melting point of either Au or GaAs, giving rise to the fusing of the GaAs NW there.

Materials excited by ultrashort laser pulses undergo different processes in comparison to that heated in equilibrium conditions. After excitation, electrons and holes are redistributed by carrier-carrier and carrier-phonon scattering. Carrier-carrier scattering causes electron and hole thermalization while carrier-phonon scattering transfers the energy of carriers to the lattice. In metals and semiconductors like the Au and GaAs, carrier-carrier scattering occurs during the first few hundred femtoseconds within the duration of the laser pulse excitation. Carrier-phonon scattering, on the other hand, takes several picoseconds before the carriers and the lattice reach thermal equilibrium. When the lattice temperature exceeds the eutectic point, melting begins to occur at the nanoparticle-NW interface region. The rest of the NW is superheated (the temperature is lower than the melting point of the NW) but remains solid until regions of liquid phase nucleate. Starting from nucleation sites at the surface, the liquid phase expands into the interior parts of the NW. However, thermal diffusion limits the expansion of the liquid region by cooling the photoexcited region. After a short period, the temperature of the liquid drops to the eutectic-related isotherm and the alloy phases begin to nucleate and finally re-solidify. Our results suggest that the melting was complete in about a hundred of nanoseconds [Figure 2].

To assess the material transport along the NW, an analysis was conducted using the following formula. The length l at which the material diffuses in the NW is given by,

$$l = \sqrt{2D\tau} \quad (1)$$

$$D = D_0 \exp\{-Q/kT\} \quad (2)$$

where l is the diffusion length within the time τ , D the thermal diffusion coefficient of Au in either GaAs or Ga, D_0 the maximal diffusion coefficient, Q the activation energy, k the Boltzmann constant, T the temperature. Taking the parameters of $T = 900$ K and $\tau = 20$ ns [Figure 2] into the equations (1) and (2), the diffusion length can be estimated. For the case of Au diffusion in GaAs, the diffusion length is only ~ 3 pm according to the values of $D_0 = 8.9 \times 10^{-9}$ cm²/s and $Q = 0.65$ eV [41]. Alternatively, based on

the parameters of $D_0 = 4.9 \times 10^{-4} \text{ cm}^2/\text{s}$ and $Q = 0.12 \text{ eV}$ [42], the Au diffusion length in Ga is ~21 nm. The diffusion lengths in these two cases, however, are smaller than that experimentally observed (~45 nm transient increase at 20 ns). It indicates that there might be a fast diffusion mechanism to account for the phenomenon observed in Figure 2.

Mass transport along the NWs would proceed by bulk diffusion and/or surface diffusion. Diffusion on the NW surface is usually associated with lower effective activation energy, and hence is faster than diffusion in the interior of the dense NW [43]. After an incoming laser heating pulse, in contrast to bulk diffusion, the Au and Ga species could diffuse a longer distance because of the surface diffusion. Therefore, owing to the low diffusion barriers at surface, phase reaction may also occur on the NW surface in addition to the Au/GaAs interface. When the temperature at the threshold laser fluence exceeds the phase reaction point, liquid phase appears toward a certain distance along the NW as a result of the fast surface transport, leading to the expansion and subsequent length increase of the NW. Because of the transient expansion necking can be seen near the Au/GaAs interface, resulting in the slight narrowing of the NW width there [second column in Figures 2a and 2b]. As the phase reactions came to a complete end, the NW length decreased due to the resolidification of the newly formed alloys [third column in Figure 2].

Our results in Figures 3 and 4 confirm that surface diffusion played an important role in the transient length increase of the NWs. Because AlGaAs and GaAs possess different surface energies [44], they would affect the diffusion of Au along the NW surface upon laser pulse heating. With the AlGaAs coating layer on the GaAs NW, surface diffusion would not be as fast as that in the core-only NW [45-47], which would not be favorable for the phase reactions to occur. Another contributing factor could be the eutectic-related temperature. Because of the addition of an AlGaAs layer, the eutectic-related condition between Au and AlGaAs became more difficult than that for the case of Au and GaAs. Therefore, the laser fluence needed for the phase reactions in the core-shell NW is much higher than that in the GaAs core-only NW [Figure 3]. In addition, the transient length increase in ZB NW but not in WZ NW [25] suggests that the crystal structure plays an important role in surface diffusion. The WZ NW has a hexagonal structure while

the ZB is cubic. It suggests that the ZB structure promotes the surface diffusion upon the laser pulse excitation, resulting in the transient increase of the NW length in contrast to that of the WZ NW.

In summary, we have used 4D electron microscopy in the study of phase reaction dynamics in polytypic GaAs NWs. The dynamics were initiated by a laser heating pulse while the subsequent appearances of the NW morphology, representing an early stage in the phase reactions, was projected by a precisely time-delayed electron pulse. The experimental findings in ZB, WZ GaAs and core-shell GaAs-AlGaAs NWs were compared. The ZB NW showed a transient length increase within ~ 150 ns and subsequent length reduction after the phase reactions had fully ended. In contrast, both the WZ and core-shell NWs did not show a transient length increase but only a small length reduction throughout the reaction process. The underlying mechanism was discussed according to the favorable material transport along the NW surfaces. 4D space-time single-pulse imaging of multi-phase involved processes have shown excellent promise in exploring irreversible dynamics at targeted positions and in unravelling underlying mechanisms in any other complex systems, with high spatial and temporal resolution.

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FIGURE CAPTIONS

Figure 1. Experimental setup for four-dimensional visualization of the phase reaction dynamics in nanostructured materials. (a) Schematic diagram of 4D electron microscopy with high spatiotemporal resolution. The green laser heating pulse enables the phase reactions of the Au/GaAs NWs to be measured by the delayed electron pulse at a given time delay. (b) Morphology of the as-grown Au/GaAs NWs. The NWs are distributed far away from each other to avoid any disturbance in the laser-induced dynamics studies. (c) Typical micrographs of the ZB GaAs NW and the GaAs/AlGaAs core-shell NW. A gold nanoparticle is located on the top of each NW.

Figure 2. Single-pulse imaging of the phase reactions in the ZB GaAs NW. (a-c) Snapshots showing the states of the NW before, at specific delay times and after the process had ended, respectively. Length increase of the NW was observed in the transient states (second column) while length reduction of the NW occurred in the final states (third column). The dotted and solid lines represent the initial and latter states of the NW tip positions. (d) Schematics showing the NW in three different stages, i.e., before, during and after the phase reaction process. Only one electron pulse is present to image the initial and final states of the NW (“before” and “end”) while an optical pulse illuminates the NW and a following electron pulse is used to take the snapshot at a specific delay time (“during”).

Figure 3. Snapshots of the phase reaction dynamics in the GaAs/AlGaAs core-shell NW. (a) Threshold laser fluence for initiating the phase reactions in the core-shell NW. Morphological changes of the NW tip can be seen in the images with notations “end” and “final”. (b) Time-resolved phase reaction dynamics in the core-shell NW. A slight reduction of the NW length was observed at 20 ns and after the reaction process had ended. The dotted and solid lines mark the NW tip positions in the initial and later states.

Figure 4. Fusing behavior of the ZB GaAs NW in the high laser fluence condition. (a) Initial NW before the laser pulse illumination. (b) Threshold fluence (5.5 mJ/cm^2) for initiating the phase reactions. (c-e) The NW length gradually decreased while the size of the top particle increased. The dark feature marked by an arrow moved downwards along the NW. (f) The NW was fused at the laser fluence of 25 mJ/cm^2 .

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Figure 1

Figure 2

Figure 3

Figure 4