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Control of defects in a novel aluminum-induced heteroepitaxial growth of $Al_xGa_{1-x}P$ nanocrystals on silicon nanowires

Qingwei Zhou,[a] Zhang Zhang,[a,*] Stephan Senz,[b] Fuli Zhao,[c] Lijun Chen,[b] Xubing Lu,[a] Xingsen Gao[a] and Junming Liu[d,*]

[a] *Institute for Advanced Materials and Laboratory of Quantum Engineering and Quantum Materials, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, People's Republic of China*

[b] *Max Planck Institute of Microstructure Physics, Weinberg 2, Halle 06120, Germany*

[c] *Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen University, Guangzhou 510275, People's Republic of China*

[d] *Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, People's Republic of China*

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Aluminum-induced heteroepitaxial growth of aluminum gallium phosphide nanocrystals ($Al_xGa_{1-x}P$ NCs) has been achieved on both silicon substrate and the tips of Al-catalyzed silicon nanowires (Si NWs). Al-induced growth is a silicon complementary metal–oxide-semiconductor compatible solution, and a growth mechanism of $Al_xGa_{1-x}P$ NCs was proposed. The decrease in structural defects in $Al_xGa_{1-x}P$ NCs grown heteroepitaxially on Si NWs was confirmed by transmission electron microscopy and Raman spectroscopy.

Keywords: Aluminum; Si nanowires; Heteroepitaxy; Nanocrystals

Most current functional semiconductor nanostructures are based on the Si platform [1,2]. There are the lattice mismatches between group III–V compounds and Si. Therefore, without a sufficiently thin mismatched interlayer to release the force by elastic surface deformation, group III–V low-dimensional nanostructures directly grown on Si substrate tend to form to relieve the strain that builds up after growth of a few layers, and the strain finally results in a kinked heterostructure. However, in semiconductor nanowire (NW) heterostructures, stress caused by a lattice mismatch can be relaxed through elastic deformation near the NW interface [3], without introducing dislocations that detrimentally influence the physical properties of these materials. Furthermore, when hereroepitaxially grown on Si substrates, self-assembled nanoislands of III–V compounds with different facets were orientation mediated [4], and the formation of facets on the nanoislands of III–V compound is believed to be the major source of the anti-phase defects [5].

Axial heterostructures, along the NW growth direction, can be achieved using normal semiconductor NW growth techniques, i.e. metal particle-catalyzed growth mechanisms [6]. Using a number of metal catalysts, semiconductor nanowires (Si, Ge, III–V compounds) have been synthesized via vapor–liquid–solid (VLS) growth [7]. However, there is a specific challenge to obtaining semiconductor NW growth compatible with complementary metal–oxide-semiconductor (CMOS) processing, as the metal catalyst behaves as a deep-level impurity contamination in Si. Contaminant Au produces a deep level close to the middle of the Si band gap with high recombination efficiency. Therefore, one of the most significant issues is the elimination of Au from the process. Since Au is difficult to remove completely after growth [8], catalysts compatible with CMOS requirements or catalyst-free growth techniques must be developed. Recently, Al as a Si-CMOS compatible catalyst for Si NW epitaxy has attracted much attention [9,10]. As it is a shallow acceptor in Si, Al acts as both a catalyst and a dopant, yielding p-type doping [11]. Gallium phosphide (GaP) has a lattice mismatch of <0.4% relative to Si, and is thus the best candidate of the binary III–V compounds for

* Corresponding authors; e-mail addresses: zzhang@scnu.edu.cn; liujm@nju.edu.cn

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investigating the initial heteroepitaxial phase formation on Si with little strain effect. $Al_xGa_{1-x}P$ is lattice matched to GaP for all Al mole ratios, and it is essential to decrease the lattice-mismatch-associated structural defects during the initial stage of heteroepitaxial growth on Si. However, there are few reports about the growth of Al-catalyzed or Al-induced III–V low-dimensional nanostructures. In this work, we report the heteroepitaxial growth of $Al_xGa_{1-x}P$ nanocrystals (NCs) on both Si substrates and tips of Si NWs using Al as a seed. The chemical beam epitaxy (CBE) growth and control of structural defects were studied using electron microscopy and Raman spectroscopy.

Top and tilted-side view scanning electron microscopy (SEM) images were used to study the Al nanoparticles before and after $Al_xGa_{1-x}P$ growth, as well as the morphology of $Al_xGa_{1-x}P$ NCs on Si substrate. Discrete Al nanoparticles after annealing are shown in Figure 1a, in which the bright contrast corresponds to the Al, and the dark one in between is the bare surface of the Si (1 1 1) substrate. Details of the experiments are presented in the Supplementary material and the process for synthesizing $Al_xGa_{1-x}P$ NCs on Si is schematically shown in Figure S1. The annealing process (600 °C for 10 min) causes a relatively large size distribution of Al–Si droplets, the mean diameter of which was measured from Figure 1a to be ~20 nm. The tilted-side view in Figure 1b confirmed that the dark hemispheres were the Al seeds with a height of 5–20 nm corresponding to different diameters. Growth of $Al_xGa_{1-x}P$ NCs was observed at each Al site and no hemisphere-shaped Al remained after CBE growth (as shown in Fig. 1c). The NCs appeared to be faceted with a large size increase (50–150 nm in diameter, 50–100 nm in height), and no typical Al seeds remained on the Si surface. However, both the size and faceting of the $Al_xGa_{1-x}P$ NCs were found to be unique. An investigation of GaP islands reported {1 1 1}-type faceting at each growth temperature and this effect was especially pronounced at 550 °C [12]. Faceting and structural defects of as-grown

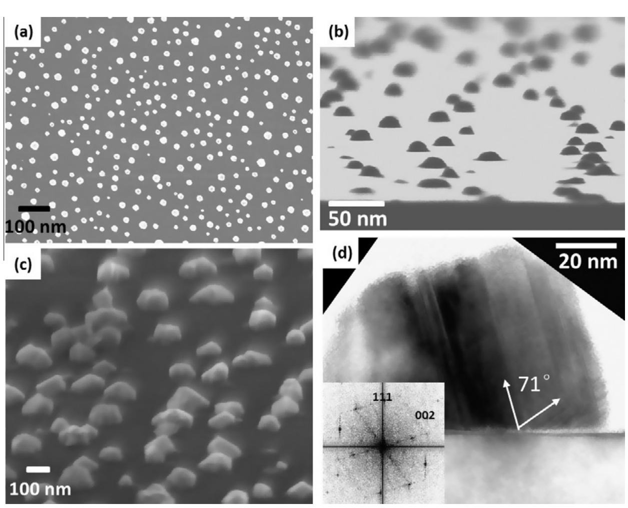

Figure 1. (a) Top view and (b) tilted-side view SEM of Al catalysts on Si(1 1 1) substrate. (c) Tilted top-view SEM image of the Al-induced $Al_xGa_{1-x}P$ nanoislands grown on a Si(1 1 1) substrate. (d) Cross-sectional HR-TEM image of a single $Al_xGa_{1-x}P$ NC viewing along the [1$\bar{1}$0] zone axis; inset shows the ED pattern by FFT corresponding to twin planes that meet at an angle of 71°.

$Al_xGa_{1-x}P$ NCs on Si substrate were analyzed. One NC with an integral cross-section on Si is shown in the high-resolution transmission electron microscopy (HR-TEM) image of Figure 1d. It is obvious that no remaining Al seed exists on the top side of the NC, or embedded on the interface with Si, confirming that this is non-catalyzed growth. Based on the volume expansion from Al nanoparticle to $Al_xGa_{1-x}P$ NC shown in Figure 1, the Al proportion x is calculated to be ~1–2%, which is similar to the value estimated from the photoluminescence spectrum (see Fig. S2). Stacking faults introduced at the early stage of heteroepitaxy were identified as dominant planar defects (see inset electron diffraction (ED) pattern by fast Fourier transform (FFT) of the TEM image in Fig. 1d). Defects in heteroepitaxial films are commonly due to lattice mismatch and thermal expansion mismatch stresses between the film and substrate during growth. However, as reported by Ernst et al. [13] in the case of growing GaP islands on Si(0 0 1), the mismatch stresses play only a minor role in the formation of planar defects and the dominant formation mechanism are atomic positioning errors on {1 1 1}-facets during the early stage of heteroepitaxial growth. Therefore, antiphase defects are important. Group III–V compound semiconductors have polar (1 1 1) surfaces with either group III or group V elements terminating the lattice. Even though a general relationship of planar defect formation mechanism and faceting cannot be obtained by investigations of a single nanocrystal, it was observed that the planar twin defects originate from the interface with the Si surface with two directions of {1 1 1} twin planes that cross at an angle of 71° (as marked in Fig. 1d). We believe that these defects were produced from interfacial defects caused by Al–Si alloy formation on Si substrate during annealing.

In order to determine the influence of the Al–Si interface on $Al_xGa_{1-x}P$ crystallization, the CBE procedures were performed using Al-catalyzed Si NWs with the same growth parameters. First, the epitaxial growth of Al-catalyzed Si NWs on Si(1 1 1) substrate was achieved via a vapor–solid–solid (VSS) growth mechanism. The top-view SEM image in Figure 2a shows that wires with diameters >20 nm prefer the perpendicular [1 1 1] growth direction, whereas wires with diameters <20 nm are mostly <1 1 2> oriented. The substrate surface is Si(1 1 1) and the stereographic projection of the <1 1 2> growth directions can be identified as depicted schematically in the inset in Figure 2a. There are three <1 1 2> directions almost perpendicular to the substrate, and six other <1 1 2> directions with proper minus sign on some indexes are almost parallel to the surface. We are looking only for standing wires, not for those grown along the surface. The cross-sectional TEM image of Figure 2b confirms that the <1 1 2> orientations are kinked ±19° with respect to the normal of Si(1 1 1). Wires with relatively smaller diameters are labeled by black dashed circles. Otherwise, wires of bigger diameters grow perpendicular to the substrate in the [1 1 1] direction as marked with white dashed circles. A [1 1 2]-oriented wire was investigated by HR-TEM. Images with different magnification are shown in Figure 2c and d. It is apparent that the growth of Si NWs is along the [1 1 2] direction with a 71° tilt relative to the surface of the Si(1 1 1) substrate. Although the wire was slightly tapered, the diameter at the base is still <20 nm.