

Synthesis of nanometer-scale boron phosphide whiskers by vapor-liquid-solid chemical vapor deposition

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Densely packed layers of boron phosphide whiskers have been grown on quartz, tungsten, and graphite substrates by chemical vapor deposition. Nickel and silver acted as liquid forming agents in a vapor-liquid-solid growth mechanism. The formed whiskers have diameters typically between 10 and 5000 nm, depending on the substrate material, the seeding metal, and the synthesis temperature. The length of the whiskers can be as large as 0.1 mm. High-resolution transmission electron microscopy imaging revealed that the whiskers are single crystalline with a large number of twin faces. © 1996 American Institute of Physics. [S0021-8979(96)08308-7]

Boron phosphide (BP) is a III-V semiconductor with an indirect band gap of 2.0 eV and a zinc-blende crystal structure.¹ As was pointed out by Kelder *et al.*,² this rather unknown semiconductor has the mechanical and chemical properties of refractory materials, such as a Vickers hardness similar to that of TiN. Recently, we investigated BP as a protecting optical window for silicon in photoelectrochemical cells.³ In that study, epitaxial BP(100) films were deposited by chemical vapor deposition (CVD) on both *n*- and *p*-type Si(100) substrates. It was shown that the conduction bands of Si and BP match quite well, whereas a potential barrier of 0.9 V is present between the valence bands of these two semiconductors.

The growth mechanism of whiskers has been a topic of intensive research for many years. To date, it is widely accepted that a vapor-liquid-solid (VLS) mechanism, as proposed by Wagner and Ellis in 1964,⁴ is most successful in explaining the highly anisotropic growth of these crystals. In contrast to growth rates in conventional heterogeneous vapor-solid film syntheses, the unidirectional high growth rate is caused by an effective supply of reactants to specific nucleation sites. Necessary for this mechanism is a liquid forming agent, like metallic impurities, on the substrate surface. At the deposition temperature (around 900 °C for BP) the precursors dissociate and dissolve into the molten Ni or Ag seeds. When saturation is reached, crystallization of the product starts at the liquid-solid interface and after awhile the formed crystallite pushes the seed metal droplet away from the substrate. Continuation of this process results in whisker formation.

Here we report on the study of thin BP films with a large physical surface area. These layers of whiskers have been synthesized on different substrates. Nanostructured semiconductor thin films have recently aroused scientific and technological interest because of the discovery of luminescent porous Si,⁵ and the remarkable success of the Grätzel-type liquid junction photovoltaic solar cells.⁶ High surface area electrodes of the chemically stable semiconductor BP may

also be applicable as gas sensor, in photocatalysis, and for energy conversion purposes. While BP whiskers can easily be obtained by CVD using VLS,⁷ little has been reported on relations between process conditions and whisker morphology. We investigated the influence of different seed metals and substrate materials, as well as the deposition parameters on the VLS-growth characteristics of BP whiskers.

Boron phosphide whiskers were synthesized in a vertical cold-wall CVD reactor (inner diameter 36 mm) using inductive susceptor heating. The precursors, BBr₃ (Alfa el. grade 99.99%) and PBr₃ (Merck Suprapur >99%), were diluted in H₂ (99.999%, Pd purified and dried) carrier gas and reacted on the substrate, which was heated to temperatures ranging from 850 to 1000 °C. Partial pressures were varied in the range of 0.2–0.5 Torr for BBr₃ and 2.0–5.0 Torr for PBr₃, flow rates ranged between 0.8 and 1.5 l/min. The substrate materials investigated were quartz, tungsten, and graphite, which were dipcoated in a 0.02 M solution of nickel or silver acetate (Baker anal. grade). In order to remove all oxygen and carbon contamination, the substrate was reduced in H₂ at 900 °C prior to the deposition. Two or three substrates, of typically 10×10 mm, were coated simultaneously in one experiment.

For high-resolution transmission electron microscopy (TEM) analysis small graphite substrates were used which could be placed into the microscope. Since the constituents boron and phosphorus both have low electron scattering cross sections, the whiskers did not need further preparation.

TABLE I. Summary of BP whisker formation on C, W, and quartz substrates. The gas-flow rates in the reactor were equal; typical deposition time was 20 min.

Substrate	Seed	Temperature	Typical diameter
Graphite	Ni	<930 °C	0.01–0.1 μm
Graphite	Ni	>940 °C	1–5 μm
Graphite	Ag	880–1000 °C	1–10 μm
Tungsten	Ni, Ag	930 °C	1–5 μm
Quartz	Ni	880–1000 °C	0.1–5 μm

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During the CVD-VLS process, layers of randomly oriented whiskers are formed. The diameter of the whiskers strongly depends on the substrate material, the seeding solution, the deposition temperature, and the deposition time. Typical axial growth rates are $0.5 \mu\text{m}/\text{min}$, whereas radial growth rates are at least two orders of magnitude less. An increase of the reactant partial pressures or flows results in higher growth rates, but does not significantly change the shape of the whiskers. Table I contains a summary of the different combinations of the substrate materials and seeding solutions that were investigated, and the typical whisker diameters obtained.

Scanning electron micrographs of the whiskers with large diameters show distinct crystal faces. At low deposition temperatures, the whiskers have hexagonal morphology [see Fig. 1(c)], whereas at high temperatures the crystals are triangular [see Fig. 1(b)]. Near the tip of the high-temperature grown whiskers, three additional faces appear, again showing the hexagonal form. The hexagonal shape in a zinc-blende crystal strongly suggests that preferred growth occurs along the (111) direction. At high growth temperatures, the side faces of the whiskers are smooth, whereas at lower temperatures, "stepped" surfaces and branching appear [see Fig. 1(c)]. High-resolution TEM pictures (see Fig. 2) reveal the crystal structure of the small-diameter whiskers. Micrographs reveal crystals which contain a high density of twin planes, spaced approximately 10–20 nm apart. Surprisingly, energy dispersive x-ray (EDX) element analysis on the whisker tips did not reveal any traces of nickel, while x rays attributed to nickel were found when the electron beam grazed the graphite surface.

Nickel or silver on the substrate surface is responsible for the growth of whiskers, because it is found that substrates which had not been treated with NiAc_2 or AgAc are covered with a dense layer of polycrystalline BP rather than whiskers. The nature of the substrate plays an important role in the whisker diameter. It influences the size of the seed, and thus the initial whisker diameter. For graphite substrates dipped into NiAc_2 , the deposition temperature dependence of the whisker diameters shows two regimes, one of small (tens to hundreds of nanometers) and one of large ($1\text{--}5 \mu\text{m}$) diameter whiskers. Since no such behavior is observed in the Ag-catalyzed depositions, the two types of whiskers are related to the specific interactions of nickel with graphite. The Ni catalyst promotes hydrocarbon formation which leads to etch pits on the substrate,⁸ preventing the sintering of Ni into larger seeds. The large-diameter regime must be caused by an increase in the seed size. A strong increase in wetting of the substrate, reported by Baker⁹ for temperatures above 1000°C in low-pressure environment, could also operate at slightly lower temperatures in our system.

For tungsten and quartz substrates, an approximate linear relationship between the temperature and the diameter is found. This behavior can be explained by the size of the droplet/solid contact area which depends on the surface tension of the droplet material. Higher temperatures reduce this tension, and the droplets flatten. While initially the whisker diameter is determined by the size of the droplet, subsequent radial growth takes place by a conventional heterogeneous

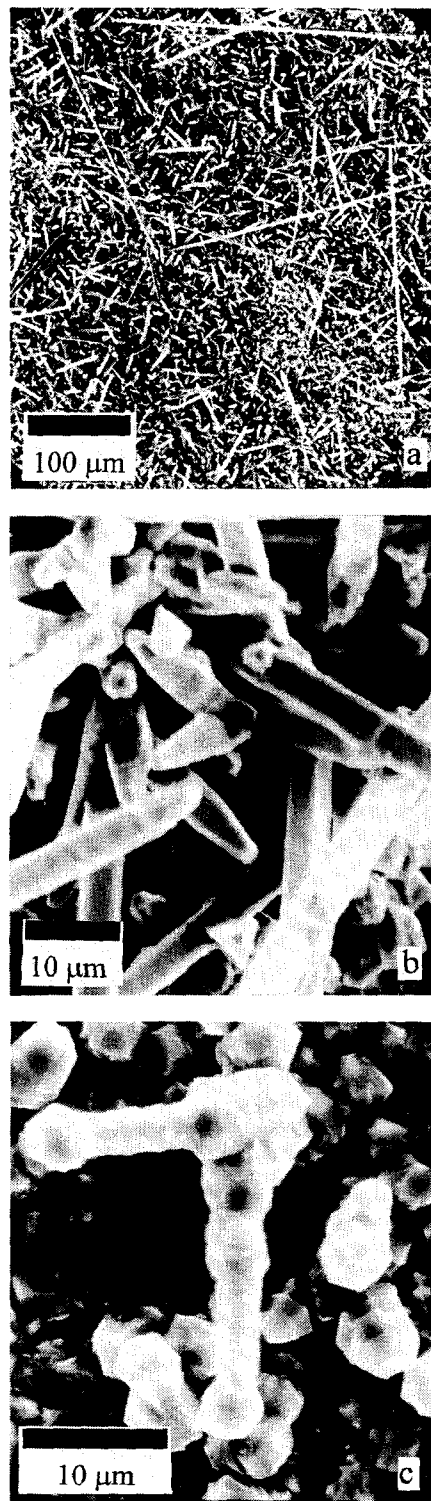


FIG. 1. Scanning electron microscope (SEM) pictures of large-diameter whiskers grown on graphite activated with NiAc_2 at 980°C (a), and 950°C (b). Stepped side faces grown at 890°C on graphite dipcoated in AgAc (c).

vapor–solid reaction mechanism which, however, is much slower than the VLS growth. Thickening of the whiskers during growth occurs only to a very limited extent.

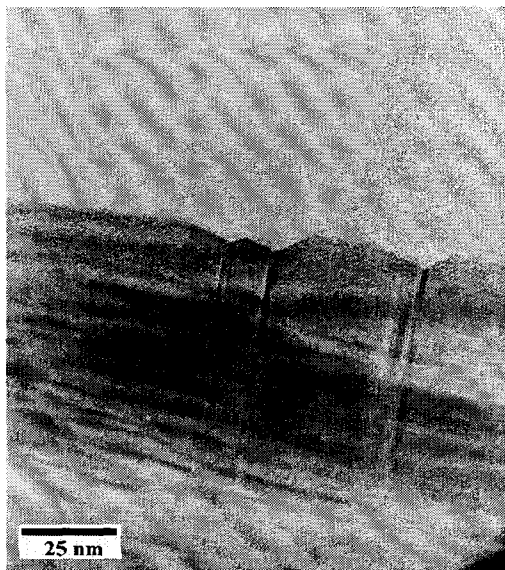


FIG. 2. High-resolution TEM picture of the side of a small-diameter whisker. Twin planes show as dark lines.

The stepped structure of the side faces of whiskers formed at low growth temperatures can be explained as follows. A periodic change in the surface tension of the liquid, due to variations in growth temperature, is expected for exothermic reactions. The droplets heat up and flatten, resulting in a larger surface, and hence an increased heat loss with subsequent temperature drop. This does not necessarily con-

verge to a stable temperature due to the changes in solubility of the species in the liquid which also influences the surface tension. An alternative explanation of the side-face morphology is the restricted surface mobility of adsorbed gas species to the side faces since higher mobilities at elevated temperatures enable the crystal to lose its surface roughness.

Whiskers of boron phosphide can be synthesized by a VLS mechanism in which nickel or silver acts as a liquid forming agent. The whiskers have typical lengths of hundreds of microns and diameters that depend linearly on temperature for quartz and tungsten substrates. For carbon substrates with Ni seeds at growth temperatures below 930 °C, the diameter of the whiskers is restricted to several tens of nanometers. The whiskers are of highly twinned single crystallinity, with a preferred growth along the (111) direction.

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