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Growth of ZnO nanowire arrays directly onto Si via substrate topographical adjustments using both wet chemical and dry etching methods

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ABSTRACT

Arrays of CVD catalyst-free ZnO nanowires have been successfully grown without the use of seed layers, using both wet chemical and dry plasma etching methods to alter surface topography. XPS analysis indicates that the NW growth cannot be attributed to a substrate surface chemistry and is therefore directly related to the substrate topography. These nanowires demonstrate structural and optical properties typical of CVD ZnO nanowires. Moreover, the NW arrays exhibit a degree of vertical alignment of less than 20° from the substrate normal. Electrical measurements suggest an improved conduction path through the substrate over seed layer grown nanowires. Furthermore, the etching technique was combined with e-beam lithography to produce high resolution selective area nanowire growth. The ability to pattern uniform nanowires using mature dry etch technology coupled with the increased charge transport through the substrate demonstrates the potential of this technique in the vertical integration of nanowire arrays.

1. Introduction

ZnO nanostructures [1,2] are an increasingly popular topic of research, finding use in areas ranging from electronics [3–5] and optics [6–9] to chemical sensing [10–12]. The material possesses a wide band gap of 3.37 eV and exciton binding energy of 60 meV [13], properties which are favorable in numerous device applications.

Much research has been conducted regarding the vapour–liquid–solid (VLS) mechanism [14] in order to achieve ideal growth of ZnO nanowires (NWs) via the use of metal catalysts. It has been further demonstrated that the metal catalyst can be selectively deposited to obtain patterned growth [15]. However, the metal catalyst particles present on the resulting NWs introduce additional contact barriers between the NW and the catalyst [16], leading to difficulties when incorporating the vertical NW arrays into existing fabrication technology [17].

To address this problem, catalyst-free growth has been achieved via the vapour–solid (VS) mechanism [18–20]. This typically requires ZnO seed layers to be deposited on a silicon substrate [21], and patterning the ZnO seed layer allows NW arrays to be selectively grown [22]. The seed layer is used to address the large lattice mismatch between ZnO (a = 3.25 Å) [23] and Si (a = 5.43 Å) [24] of 40%. As a result, the tensile stress which would exist between ZnO and Si is removed [25], providing viable conditions for ZnO vapour to nucleate directly onto the seed layer. Conduction through the base of the NW array necessitates transport of charge carriers through the seed layer, which is typically polycrystalline. Grain boundary scattering in this region and at the NW array/seed layer interface may therefore inhibit charge transport. An alternative technique allowing nucleation of ZnO directly onto the substrate leads to the avoidance of these problematic interfaces.

It has been shown that topographical alterations to the substrate surface can be used in order to promote NW growth during thermal evaporation. A proposed mechanism for increased nucleation involves surface irregularities present on the substrate acting to limit the free movement of adsorbed Zn atoms, due to the increased energy barrier associated with migration across the surface [26,27].

Previous studies have focused on substrate roughening using mechanical methods and wet chemical etching. The degree of process control using the above methods is limited, with little work carried out on the optimization of etching parameters to obtain high quality NWs. The resulting growth on Si exhibits poor

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alignment compared to seed layer grown NWs. The degree of residual contamination present on the substrate following mechanical and wet etching techniques, and the effect of this on subsequent NW growth, is also unclear [27,28].

In this study, catalyst-free ZnO NW growth is achieved and enhanced through topographical alterations to the substrate surfaces, by both wet chemical and dry plasma etching. Using this approach, single crystal ZnO NWs are grown directly on a Si substrate without the use of seed layers, avoiding boundaries present at the seed layer interface. The use of mature dry etching technology allows a high degree of process control and the ability to pattern NW arrays on a wafer scale. Also, as a subtractive process, the need for subsequent fabrication steps associated with additive seed layer patterning is avoided. Systematic optimization of dry etch parameters allows for an improvement in NW growth for vertical integration. The study was conducted on Si (1 0 0) due to its prevalent use in the semiconductor industry. The implementation of wet chemical etching provides a comparison to the previous etching related studies performed by Ho et al. Using the novel dry plasma etching method developed in this work, superior manipulation of surface topography is possible, allowing for greater control of NW growth.

The substrate topography was studied using atomic force microscopy (AFM) [29], providing information on topographic features and surface roughness. Following NW growth, crystalline and optical properties were investigated using electron microscopy, X-ray diffraction and photoluminescence spectroscopy.

2. Materials and methods

Both wet and dry (plasma) etching recipes were studied systematically, with the viability of each etch recipe determined from SEM analysis of the resulting NW growth.

Wet chemical etching of Si was conducted using potassium hydroxide (KOH) solution with concentrations of 20% and 50%, w/w. The Si substrates were suspended in the KOH solution, which was stirred continuously at temperatures ranging from 50 °C to 80 °C. Etching was performed for durations ranging from 30 s to 20 min.

Dry anisotropic etching of Si was performed using fluorine based chemistry in an Oxford Instruments Plasma Lab 80+ reactive ion etching (RIE) system. Specifically, etching plasmas containing SF_6 and CHF_3 were employed, which have been shown to proportionally increase and decrease resulting surface roughness respectively [30,31]. It has also been demonstrated that the addition of O_2 drastically increases the number of fluorine radicals, and consequently the etch rate, by preventing recombination of reaction products to form SF_6 [30]. As the concentration of oxygen atoms is increased, the etch rate begins to decrease due to increased competition from chemisorbed oxygen on the Si surface. Increasing RF power results in a higher etchant ion flux on the substrate surface, leading to an increased etch rate [32]. However, the surface roughness reaches a maximum and decreases at sufficiently high etch rates. Reaction chamber pressure also has an effect on the scale of the surface roughness, although the relationship is less well understood [33]. In summary, the parameters considered were SF_6, CHF_3 and O_2 flow rates, chamber pressure, RF power and etch duration.

A systematic approach was taken to optimize each etch recipe, with poorly optimized etches leading to uncontrolled growth of nanostructures or NWs exhibiting no significant alignment, non-hexagonal termination and large variations in dimension. More successful etch recipes resulted in NW arrays which exhibited a degree of vertical orientation and were crystallized in the wurtzite phase. In this work, one sample from each of these optimized recipes was analyzed. Details of the sample processing are displayed in Table 1, with a sample of unprocessed Si used as a basis for comparison.

Following etching, selected substrates were analyzed using AFM (JPK NanoWizard II). Scans were conducted in intermittent contact mode, using a tip with a radius of curvature of 20 nm in ambient conditions. Several 10 μm × 10 μm scans were performed on each substrate, with surface roughness values (average, RMS and peak to valley) averaged over 1 μm × 1 μm areas.

X-ray photoelectron spectroscopy (XPS) was implemented to identify the presence of contaminating species introduced by the various etching procedures. An ESCALAB XPS system (base pressure 5×10^{-10} mbar) was used, and the samples were scanned using Al K_α radiation with a pass energy of 50 eV.

Zinc oxide NWs were grown on the etched substrates using the standard double tube furnace procedure [34]. The source powder and substrates were inserted into a quartz tube, which was then inserted into the alumina furnace tube. The source material, containing a mixture of ZnO and graphite mesh, was maintained at 1050 °C, with the roughened Si substrates positioned further downstream at a temperature of ~600 °C. The process was maintained at a pressure of 1.6 mbar throughout the growth, with a gas flow of 100 sccm of Ar and 10 sccm of O_2 and a total growth time of 1 h. The NW dimensions were measured using scanning electron microscopy (SEM; Hitachi S-4800).

Crystallographic information was gathered using a Panalytical X'Pert Pro MRD x-ray diffractometer equipped with a Cu K_α hybrid monochromator. Typical 2θ measurements were performed to characterize the crystal structure of the NW arrays. XRD pole figures were subsequently produced to demonstrate the alignment of the NW array relative to the substrate normal. These measurements involve performing a coupled scan over the standard XRD angles χ and φ at constant 2θ, selected to coincide with the peak corresponding to reflection from a particular crystallographic plane. As the measurement concerns the alignment of the NWs, the (0 0 0 2) was selected as it is the vertically terminated facet of the NW.

High resolution crystallographic images were collected using a Philips CM200 FEGTEM Field emission gun TEM/STEM with Supertwin Objective lens. This was used to investigate the interface between the NW and the Si substrate.

To examine the NW optical defects, photoluminescence spectra were obtained at room temperature using a 325 nm He–Cd laser with an output power of 7 mW. The samples were illuminated at a power density of approximately 230 mW cm^{-2}.

Electrical characterization of each NW array was achieved using contact IV measurements. The bottom of each substrate was electrically bonded to a metal contact plate and a tungsten (W) tip was placed in contact with the NW array. This was performed in ambient conditions using a standard IV probe station and used to measure the conduction through the IV sweeps were performed using a Keithley 2636B source measure unit, varying the potential applied to the W tip with the substrate contact plate connected to ground.

For later comparison, zinc oxide seed layers were deposited at a thickness of 20 nm using room temperature RF magnetron sputtering (Lesker PVD 75), employing an Ar/O_2 gas mix (10:1) in order to retain stoichiometry.

3. Results and discussion

3.1. Comparison of NWs grown on etched Si

Fig. 1 shows SEM images of the NW growth, with corresponding AFM scans of the substrate surface. It is apparent that the surface topography is inherently different for each etch recipe used, yielding NWs with differing morphology and orientation. Surface