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The effect of doping on low temperature growth of high quality GaAs nanowires on polycrystalline films

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Abstract

The increasing demand for miniature autonomous sensors requires low cost integration methods, but to date, material limitations have prevented the direct growth of optically active III-V materials on CMOS devices. We report on the deposition of GaAs nanowires on polycrystalline conductive films to allow for direct integration of optoelectronic devices on dissimilar materials. Undoped, Si-doped, and Be-doped nanowires were grown at $T_s=400^\circ\text{C}$ on oxide (indium tin oxide) and metallic (platinum and titanium) films. Be-doping is shown to significantly reduce the nanowire diameter and improve the nanowire aspect ratio to 50:1. Photoluminescence measurements of Be-doped nanowires are 1–2 orders of magnitude stronger than undoped and Si-doped nanowires and have a thermal activation energy of 14meV, which is comparable to nanowires grown on crystalline substrates. Electrical measurements confirm that the metal-semiconductor junction is Ohmic. These results demonstrate the feasibility of integrating nanowire-based optoelectronic devices directly on CMOS chips.

Introduction

Wireless sensor networks are the backbone of the evolving system of interconnected commercialized devices known as the Internet of Things.[1] These networks are comprised of low power sensor nodes utilized in smart appliances, environmental monitors, and implantable biomedical devices.[2–4] Millimeter scale sensors have already demonstrated energy-autonomous operation using photovoltaic cells in conjunction with both solar [5–7] and indoor lighting.[8] Incorporation of optoelectronic devices into wireless sensor nodes is currently achieved externally by wire bonding separate components into a stacked unit.[5,9] Integrating silicon CMOS and III-V optoelectronic devices as a single component would eliminate the need for wire bonding and decrease the thickness. Material incompatibility, especially between the Si-based logic circuits and the GaAs-based optoelectronics, limits this approach due to defects formed between dissimilar materials. [10,11] There has been some success using lattice engineered substrates [12], flip-chip [13] and fluidic self-assembly methods [14], but the amount of processing and thus the cost required for these techniques is excessive for most applications.

We propose to integrate these devices by using self-assembled nanostructures. Nanowires will act as the active region of the optoelectronic device and will be grown directly on the surface of the pre-packaged sensor. The nanowires can be grown on either an exposed metal pad, or subsequently deposited conducting films. It has already been demonstrated that nanowires can be used to create light emitting diodes [15–19] and solar cells with a fraction of the material. [20–24] To enable on-chip nanowire growth, sufficiently high quality nanowires have to be deposited directly on polycrystalline conductive layers at temperatures at or below 400°C to prevent degradation of metallic interconnects.[25] GaN nanowire LEDs have been grown on metallic films with great success but requires substrate temperatures of 800°C. [26, 27] GaAs nanowire growth by vapor deposition has previously been demonstrated on polycrystalline films with mixed results.[28–31] In some reports the nanowires have a high aspect ratio with full surface coverage, but in others the nanowires are sparse and misshapen. Here we present on the growth of GaAs nanowires on polycrystalline conducting films at 400°C. We investigate the impact of doping and growth rate on the nanowire density and morphology. We find that the structural and optoelectronic quality can be improved with Be dopants. Be doped nanowires have a high aspect ratio (50:1), a reduced number of stacking faults, and strong room temperature photoluminescence. We believe this study presents a significant step forward towards the direct integration of III-V devices on CMOS technology.

Growth Details

The maximum growth temperature possible for integrating nanowires with CMOS was found by heating sensors containing wire-bonded stacks of Si devices developed by Blaauw et al. [5–7] in a molecular beam epitaxy chamber, after which they were tested for functionality and electrical conductivity. These samples were heated to 300, 400, and 500°C and annealed for 30 minutes and removed. Devices annealed to 500°C exhibited open circuit responses whereas samples heated to 400°C and 300°C remained functional, consistent with other CMOS temperature studies. [25] Thus, all subsequent nanowire growths were conducted at substrate temperatures of 400°C.

Three polycrystalline films were examined as substrate candidates, indium tin oxide, platinum, and titanium. For the samples with ITO films, oxide-free p-doped silicon substrates were coated with 100 nm of ITO at room temperature at rate of 1.8 A/s with 40sccm Ar and 1sccm O₂ at 139W of DC power. For samples with Pt films, Pt/TiO/Si/SiO₂ substrates were purchased from Radiant Technologies. For samples with Ti films, 4nm of titanium was e-beam deposited on oxide-free Si wafers using an Enerjet system.

Each substrate was coated with a thin film of Au to act as the catalyst necessary for nanowire growth. For both ITO and Pt films, 5nm of Au was sputter coated at room temperature under 5 mTorr vacuum for 16s with the Ar plasma at 18V. For the Ti film, 5nm of Au was deposited using e-beam deposition immediately after Ti deposition. This both prevents Ti oxidation and acts as the catalyst for nanowire growth.

The GaAs nanowires are grown using molecular beam epitaxy chamber using the well known Vapor-Liquid-Solid (VLS) mechanism.[32] GaAs growth without an Au catalyst

resulted in the growth of a rough film and no nanowires. Samples were heated to 400°C, after which they were exposed to an As₄ flux. To initiate growth, Ga was introduced at a rate either 0.8 or 1.3 monolayers/second (ML/s). The ratio of As₄/Ga beam equivalent pressures was 10 in all growths. Growth times varied between 5 to 60 minutes. RHEED measurements show a quick transition from the ringed diffraction pattern of the polycrystalline substrate, to a complete loss of signal associated with scattering from the random array of nanostructures. Si and Be elemental sources were used as n and p type dopants as indicated, using fluxes that result in Si and Be doping concentrations of $4 \times 10^{19}/\text{cm}^3$ in planar GaAs films.

Results and Discussion

Figure 1a–c shows scanning electron microscope (SEM) images of nanowires grown on indium tin oxide (ITO), a conductive oxide widely used as a top contact in photovoltaic applications due to its transparency. These micrographs show that the nanowires grow in many different directions, forming a dense forest. The nanowires are heavily tapered and often end in a sharp point. This type of tapered morphology is also seen in GaAs nanowires grown on crystalline substrates. [33,34] Figure 1b is a cross sectional image of the sample in Fig. 1a. The majority of nanowires extends in a direction not parallel to the surface normal, and varies in length. A higher density of short and thin nanowires is present near the GaAs/ITO interface. Figure 1c is a higher magnification image of the GaAs-ITO interface (indicated by the dotted line), and shows a layer of continuous GaAs at the base of the nanowires. Energy dispersive electron X-ray spectroscopy on the continuous film above the ITO layer in Fig. 1c confirms that it is GaAs. In all of the samples measured both nanowires and the continuous film are present.

The variation in the nanowire angle with respect to the substrate exhibited in Fig. 1 may have one of two causes, epitaxial or random nucleation. An epitaxial relationship between the polycrystalline ITO and GaAs is improbable given the 79% lattice mismatch between them [35,36]. Rather, the nanowire growth is likely initiated by random nucleation events at the catalyst-film interface. Initially the angle of the nanowires is expected to be random with respect to the substrate normal and is responsible for the variation in nanowire heights in Fig. 1b. As the nanowires continue to increase in length, those growing at shallow angles will tend to terminate either by impinging on, or becoming shadowed by other nanowires. Collisions with growing nanowires can be seen in Fig. 1c. This explains why there are very thin and short nanowires near the substrate. The tapering observed in Fig. 1 is likely from a combination of sidewall growth and a shrinking catalyst, which are both well-documented phenomena in molecular beam epitaxy growth of undoped and Si-doped GaAs nanowires. [37–42]

Figure 2 plots the nanowire forest height, nanowire growth angle, and continuous layer thickness of GaAs nanowires grown on ITO as a function of growth time. The forest height, defined as the upper limit of the perpendicular distance between the nanowire tip and the substrate, has a strong positive linear correlation to the growth time ($R^2 = 0.992$), as expected. Figure 2b is a box and whisker plot showing the distribution of the angle between the nanowires and the underlying substrate. A minimum of thirty nanowires was measured

on each sample. The range (denoted by the error bars) of the distribution decreases with deposition time, consistent with the fact that nanowires with shallow angles impinge on other nanowires or are shadowed by tilted nanowires. The interquartile range (denoted by the box) also decreases with deposition time, signifying a reduction in nanowire angle variation. After an hour of growth, the median nanowire angle converges towards $\sim 70^\circ$. This convergence is somewhat surprising, because if all growth directions were equally possible, the distribution should center around 90° . However, an angled direction presents a larger capture surface for the impinging flux allowing tilted nanowires close to the surface normal to grow faster. Figure 2c shows the thickness of the continuous film as a function of growth time. The film thickness increases with growth time and saturates at a thickness of 230nm. This behavior suggests that the continuous film is not a precursor to nanowire growth, but a competitive process. As the nanowires get longer, the impinging flux is captured by the nanowires as opposed to reaching the continuous layer.

Figure 3 shows the effect of incorporating dopants into the growth of nanowires on ITO. Figure 3a is an SEM image of undoped GaAs nanowires deposited for 15 minutes. The nanowire density is nominally 10^9 cm^{-2} and as before, the nanowires extend in random directions and are heavily tapered. The overall morphology of Si-doped nanowires (Fig. 3b) is similar to the undoped wires with a nanowire density of on the order of 10^8 cm^{-2} , except that some nanowires are curved with rough sidewalls (indicated in Fig. 3b with arrows). Because they consistently curve towards the surface, it is likely that this curvature arises due to the fact that the sidewall facing the impinging flux grows more quickly than the opposite sidewall. Furthermore, the side of the nanowire on the outside of curve tends to be very rough (arrows in Fig. 3b). It is known that Si doping decreases both the Si and Ga vacancy diffusion coefficient in bulk GaAs,[43,44]. In nanowires, dopant incorporation is dominated by diffusion on the sidewalls as opposed to dissolution within the catalyst.[45] Thus, Si-doping would be expected to reduce diffusion on the sidewalls, promoting lateral growth of the nanowires.

Be-doping (Fig. 3c) leads to an increase in nanowire density (to $2.5 \pm 0.6 \times 10^9 \text{ cm}^{-2}$), a reduction in nanowire diameter, and an increase in nanowire forest height (to $2.2 \pm 0.2 \mu\text{m}$). These nanowires are less tapered, and tend to be aligned more closely to the surface normal. We propose that the Be dopant may have a surfactant effect on the nanowire sidewalls, improving the diffusion of Ga and As. This behavior has been observed for sulfur atoms during the growth of GaSb nanowires.[46]

Transmission electron microscope (TEM) measurements also show that the microstructure of the nanowires varies with doping. The TEM samples were made by removing the nanowires from the substrate and dispersing them on a grid. Figure 4a is a collection of transmission electron microscope images used to form a single image of an undoped nanowire. The nanowire has very rough sidewalls, evidence of stacking faults, tapering, and ends in a sharp point. There is no evidence of the Au catalyst anywhere along this nanowire. Figure 4b is a high resolution image of the same nanowire, and confirms the presence of multiple stacking faults and rough sidewalls. These observations are consistent with prior reports of the consequences of Au-migration, namely roughened sidewalls and tapering.[37] The observed nanowire morphology may also be due to the low temperatures of these

growths, which is also known to induce tapering. [47–49] The corresponding diffraction pattern demonstrates that the crystalline structure is wurtzite, as expected.[50] It has been shown that crystallographic phase is heavily impacted by the contact angle of the catalyst on the substrate and initial droplet radius, independent of the substrate. Namely, catalysts that are less than 25.5nm in diameter induce the formation of the wurtzite crystal structure. [51,52] This is consistent with nanowire width measurements at the apex near the catalyst ($22 \pm 5\text{nm}$) in Fig. 3c. Figure 4c shows a low resolution TEM image of a single Si doped nanowire. The nanowire is curved and no catalyst is visible along this nanowire. The catalyst may have migrated from the apex of the nanowire, contributing to the tapered morphology. This type of catalyst migration has also been observed in other nanowire growths. [37,38] The sidewalls are uneven and there are regions of the nanowire with different widths. Figure 4d is a high resolution image of the same nanowire. This image confirms the rough surfaces at the sidewalls of the nanowire. Also visible is a series of stacking faults. Regions such as these are common along the length of the nanowire, but there are fewer than the in undoped nanowire. The crystal orientation of this nanowire was also wurtzite as indicated by the diffraction pattern. Figure 4c is a low resolution image of single Be doped nanowire clearly showing the Au catalyst at the nanowire tip. Furthermore, the sidewalls appear smooth and the diameter unchanging along the length of the nanowire. Earlier we proposed that the smooth sidewalls are caused by the Be dopants having a surfactant effect on the sidewalls of the nanowire. We also propose that this surfactant effect may be preventing the migration of the Au catalyst from nanowire apex. A stable catalyst would also prevent nanowire tapering, as observed in Fig 3c. Figure 4d is a high resolution image of a single Be doped nanowire and its corresponding diffraction pattern. A few stacking faults are visible in this image, and the sidewalls are smooth. As with the undoped and Si doped nanowire, the diffraction pattern indicates that the crystal structure is wurtzite.

Figure 5a–c shows photoluminescence measurements of nanowire forests still attached to the substrate carried out at 10K with a 633nm HeNe laser with an output power of 1mW and a spot size of $5\mu\text{m}^2$. Undoped nanowires have weak peak response at 1.52eV (FWHM= 45 meV) superimposed on less intense broad emission (Fig. 5a). The position of 1.52 eV is expected for GaAs but the cause of the broad background emission is not clear. The Si doped nanowires emit a weak broad peak at 1.41 eV (FWHM= 210 meV)(Fig. 5b), which may be emission from a radiative defect caused by either Si or GaAs. Alternatively, emission in this range has previously been attributed to zinc-blende and wurtzite heterojunctions within GaAs nanowires [53]. Be-doped nanowires have an optical response that is approximately 25 times stronger, with a major peak at 1.50eV (FWHM=41 meV) and a secondary peak that is 20% as intense at 1.57 eV (FWHM=31 meV) (Fig. 5c). The 20 meV redshift of the primary peak likely corresponds to the Be-doping level and is consistent with other published PL measurements of Be-doped GaAs.[54,55] The secondary peak at 1.57 eV could either be the result of quantum confinement or a Burstein-Moss effect.[56–59]. In order for this 70 meV blue shift to arise from quantum confinement, the nanowires would have to be on the order of 10 nm in diameter. While the diameter average of the nanowires in these samples is $40 \pm 10\text{ nm}$, there is a small population of nanowires $< 15\text{nm}$ in diameter near the substrate-nanowire interface. In order for the blue shift to arise from the Burstein-Moss effect, the doping concentration would have to be approximately $9.2 \times 10^{19}\text{ cm}^{-3}$.

While it is difficult to quantify the dopant concentration in the nanowires themselves, the doping flux used in these experiments is high enough to make a Burstein-Moss related blue shift feasible.

The inset in Fig. 5c shows current density (J) vs. voltage (V) measurements of Be-doped nanowires on ITO. Be doped nanowires were used because of their superior structural and optical characteristics. To perform electrical testing, the GaAs nanowires were backfilled with parylene, followed by the e-beam deposition of 10nm of Ti and 100nm of Au to act as a top contact. To ensure a strong connection between the nanowires and the top contact, the sample was annealed at 300°C for 1 minute and without this step there is an open circuit. A bottom contact was formed similarly on the backside of the Si wafer. The rectifying response in the IV curve at positive and negative voltages presented in Fig. 5c signifies that the nanowires and ITO substrate form a Schottky contact. This is unsurprising as ITO is known to form a Schottky contact with p-type GaAs. [60]

The growth of nanowires on polycrystalline metallic films that would form an ohmic contact with GaAs were also explored. Figure 6 shows top down SEM images of nanowires grown on Pt. Figure 6a is a plan-view SEM image of nanowires grown under identical conditions as those in Fig. 1. While there is a small number of tapered nanowires of varying sizes, the majority of the substrate is covered by a rough contiguous film, likely the result of planar polycrystalline GaAs growth similar to the continuous film observed in Fig. 1c. The difference in the morphology between the two substrates is likely related to changes in the relative surface energies of the catalyst, conductive films, and GaAs. Nanowire formation via the VLS growth mode requires that the catalyst forms isolated droplets on the surface. At growth temperatures of 400°C, the deposited Au film is a solid, but because it forms a eutectic alloy, it melts upon the introduction of Ga.[61] ITO has a lower surface energy (0.02–0.03J/m²)[62,63] compared to Au-Ga (1.15 J/m²),[64] resulting in dewetting of the catalyst. Pt, on the other hand, has a much higher surface energy (2.3–2.8 J/m²)[65,66], thus exhibits a decreased tendency for droplet formation. The catalyst may be comprised of more complex alloys, namely Au_xPt_yGa_z or Au_xIn_yGa_z, that could also impact the relative surface energy.

A higher Ga deposition rate is found to overcome this limitation and allow for nanowire formation. Figure 6b is a plan-view SEM image of nanowires on Pt grown at a higher Ga deposition rate (1.3 ML/s). In contrast to the sample grown at the lower Ga deposition rate (0.8 ML/s) seen in Fig. 6a, the highly tapered and randomly angled nanowires in Fig. 6b completely cover the substrate surface. We propose that the faster deposition rate promotes random perturbations in the thickness of the catalyst layer, also called a Mullins-Sekerka instability,[67] that can lead to the formation of distinct droplets that in turn catalyze nanowire growth. The effect of dopants on the nanowire shape is similar for these samples as for those grown on ITO. Figure 6c is a plan-view SEM image of GaAs nanowires doped with Si deposited at a high rate on Pt. Here, the nanowire density is somewhat lower than for the undoped samples, suggesting that the addition of Si inhibits nanowire growth. The addition of Be results in very thin, randomly angled nanowires forming a dense forest (Fig. 6d). Occasional curved nanowires are observed in all of the samples grown on Pt.

Nanowire growth was explored on Ti as well. Figure 7 shows the characterization of Be-doped nanowires grown on Ti. Nanowire growth on Ti behaved similarly to Pt, as evident from the cross-sectional SEM image (Fig 7a). Figure 7b depicts the current density characteristics of Be-nanowires on Ti films. The samples were prepared for IV measurements in an identical manner to the samples with ITO films. The IV curve for the nanowires grown on Ti is linear at positive and negative voltages, meaning the Be-GaAs nanowires form an ohmic connection with the Ti film. This is promising for the development of nanowire based optoelectronic devices on polycrystalline substrates.

Given their Ohmic contact with the underlying substrate, Be doped nanowires grown on Ti were measured optically using temperature dependent photoluminescence to better assess their quality (Fig. 7c). The undoped and Si doped nanowires did not exhibit a strong enough photoluminescence response for room temperature measurements. Primary peaks at 1.50 (labeled as peak 1 in Fig. 7c) and 1.57 eV (peak 2) at 10K shift to 1.41 and 1.50 eV at room temperature. The intensity decreases and the peaks become less defined with increasing temperature. The 1.50 and 1.40 peak at 10K and room temperature respectively correspond to the p-type GaAs. [54,55] Similar to Fig. 5c, it is believed that the higher energy peak is the result of either a Burstein-Moss effect or quantum confinement. In the case of nanowires grown on Ti, this higher energy peak is significantly more pronounced. The position of this peak at room temperature is identical to that of another study of GaAs nanowires in which the optical emission of single nanowires are measured for quantum confinement. [56] The fact that there is a strong optical response at room temperature suggests that these nanowires are of sufficient quality to be used in optoelectronic devices. Compared to single nanowire measurements, our photoluminescence peaks are slightly broadened as they represent an average of the nanowire forest. [68]

Figure 7d shows the temperature dependence of the emission energy of peaks 1 and 2. The trendlines were calculated using the Varshni equation, for bulk GaAs, but modified with different energies at $T=0K$ (E_{G0}). [69] The energy positions of the both peaks decrease with increasing temperature and closely follow the calculated trendline. This close correlation suggests the nanowire features represented by peaks 1 and 2 have a similar temperature dependence to bulk GaAs. This is expected and provides evidence for similarities between the nanowires and single-crystalline bulk GaAs.

Figure 7e shows the plot of $I_0/I - 1$ vs $1/T$, where I_0 is the integrated photoluminescence intensity extrapolated at $T=0K$ and I is the integrated photoluminescence intensity at temperature T , in order to determine the thermal activation energy for exciton formation (E_A). At temperatures above 50K we see quenching of the intensity, corresponding to an E_A of approximately 14meV. For comparison, nanowires grown near 600°C at GaAs and Si crystalline substrates have been reported with high temperature E_A of 17meV and 77meV respectively. [68,70]. This suggests that the Be doped nanowires presented in this study are comparable to those grown at high temperatures on crystalline substrates.

In summary, we have been able to demonstrate that Be doping can enable the growth of high quality GaAs nanowire growth at low temperatures on polycrystalline films. Among other applications, this will allow for direct integration of nanowire-based optoelectronic devices

with conventional CMOS technology. We demonstrate that nanowires can be grown on polycrystalline ITO, Pt and Ti films, but believe the process can be applied to other oxide and metallic surfaces. Growth on polycrystalline substrates will cause nanowires to grow in random directions, which can result in termination events, reducing nanowire density. We show that by growing with Be, the nanowires tend to grow more closely to the surface normal directions, and the nanowire quality is greatly improved. The nanowires have a thermal activation energy of 14 meV which is comparable to GaAs nanowires grown on crystalline substrates and at higher temperatures. A greater understanding of the dopant interactions and development of a p-n junction is necessary and the direction of future work.

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Figure 1.

a) Top down and b) cross sectional scanning electron microscope (SEM) images of GaAs nanowires grown on indium tin oxide (ITO) for 30 minutes. c) High magnification SEM image of the GaAs-ITO interface, with the interface between the ITO and GaAs (dotted line) indicated.

Figure 2. Statistical measurements of nanowire samples grown on ITO with growth times between 5 and 60 minutes. a) Nanowire forest height, b) nanowire growth angle and the c) continuous film thickness are measured.

Figure 3.

Cross-sectional SEM images of GaAs nanowires grown on ITO for 15 minutes with a) no doping, b) Si doping, and c) Be doping. Photoluminescence measurements for the samples shown in a-c are performed at 10K, and the intensity is normalized. The intensity scale is linear.

Figure 4. Transmission Electron Microscope images and diffraction patterns of a–b) undoped and c–d) Si doped and e–f) Be doped GaAs nanowires grown on ITO.

Figure 5. Photoluminescence data of nanowires grown on ITO with a) no doping, b) Si doping, and c) Be doping. d) Current-Voltage measurements of Be doped nanowires.

Figure 6. Plan-view SEM images of GaAs nanowires grown on Pt films at a) low Ga fluxes (6×10^{-7}) and b) high Ga fluxes (9×10^{-7}) along with the addition of c) Si and d) Be dopants at the higher deposition rate.

Figure 7.

a) Cross-sectional SEM images of Be-doped GaAs nanowires grown for 30 minutes on a Ti film. b) I–V characteristics of Be-doped nanowires on Ti c) Temperature dependent photoluminescence of Be-doped nanowires on Ti. The d) position and e) intensity of peaks 1 and 2 are plotted against temperature.