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Graphene mediated growth of polycrystalline indium phosphide nanowires and monocrystalline-core, polycrystalline-shell silicon nanowires on copper

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ABSTRACT

Two types of semiconductors, indium phosphide (InP) and silicon (Si), were separately grown on polycrystalline copper foils with the presence of gold colloidal particles. InP was grown with and without carbon deposition by metal organic chemical vapor deposition, and Si was grown with and without plasma enhanced chemical vapor deposition of carbon. While InP and Si grew as films on untreated copper foils, they were found to grow in the form of nanowires when copper foils were pre-treated with carbon. Structural analysis revealed that the grown InP nanowires were polycrystalline. In contrast, the grown Si nanowires were found to have core–shell structures with a monocrystalline core and a polycrystalline shell. Further analysis suggested that graphene was formed on the copper foils during the carbon deposition. Therefore, we concluded that the presence of graphene promoted the growth of InP and Si in the form of nanowires. The demonstration of growing semiconductor nanowires on copper foils could be a new path to integrate semiconductor and metal to provide a unique material platform for a wide range of devices.

1. Introduction

There are many potential applications, such as optoelectronic and thermoelectric devices, which would benefit from utilizing low cost metallic substrates, such as flexible metal foil substrates, for the growth of semiconductors. Aluminum and copper, for instance, are low cost materials with excellent electrical and thermal conductivity, making them suitable electrode materials for devices. Heteroepitaxial growth of metal on semiconductor surfaces has been extensively studied to develop high performance electrodes [1] although it is also been demonstrated that polycrystalline, rather than single-crystal, metal films simply deposited on semiconductor surfaces serve as acceptable electrodes [2,3]. In contrast, growth of semiconductor materials directly on metallic surfaces has been limited to non-single crystal (i.e., polycrystalline and amorphous) semiconductor films, [4,5] presumably because of the lack of demand for epitaxially grown single-crystal semiconductors on metallic surfaces. For this reason, even emerging semiconductor nanostructures such as quantum dots and nanowires are almost exclusively grown on single-crystal semiconductor substrates, [6,7] with a few exceptions demonstrated on non-single crystal semiconductor surfaces [8–10]. InP nanowires grown using copper seeds have been demonstrated; however, the demonstration involved a single crystalline InP substrate [11]. New demonstrations were recently reported, in that, graphene enabled epitaxial growth of InAs nanowires on copper and InGaAs nanowires on MoS_2 surfaces [12,13].

One of the main fields that would benefit from the growth of semiconductor nanostructures, such as our nanowires on polycrystalline copper, is thermoelectric devices. One of the key reasons for designing semiconductor nanowire thermoelectric devices is to utilize the electron transport properties of nanowires to maintain a preferred electrical conductivity via quantum effects, i.e., ballistic transport [14,15]. More importantly, rough surfaces of nanowires allow the scattering of phonons, therefore reducing thermal conductivity, which is another important aspect to increasing thermoelectric efficiency [16,17]. In fact, phonon scattering has proven so essential to thermoelectric efficiency that polycrystalline materials, which scatter phonons with a much

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higher efficiency than that in monocrystalline materials, show promise as a viable thermoelectric material platforms [18,19]. In polycrystalline materials containing grains with various sizes ranging from 3 nm to 1 μm, phonons with a wide range of wavelengths may be scattered efficiently, therefore increasing thermoelectric efficiency [19]. Additionally, grain boundaries can scatter phonons [20]. From these preliminary demonstrations and design considerations, we concluded that it is logical to use polycrystalline materials in the form of nanowires for thermoelectric devices, in order to combine the benefits provided by both polycrystalline films and nanowires to achieve maximum phonon scattering.

In this study, InP and Si were chosen to further study graphene's role in promoting the growth of semiconducting nanowires, including group IV semiconductors. In pursuing the growth of semiconductors on metallic surfaces, our study explores a method to grow semiconductors in the form of nanowires on polycrystalline copper foils, using graphene as an intermediate layer. InP nanowires are entirely polycrystalline while the Si nanowires have monocrystalline-core and polycrystalline-shell structures. These material platforms could offer unique benefits to engineer thermal and electrical conductivity for thermoelectric devices.

2. Experiment

Four samples were prepared on mechanically flexible, non-single crystalline copper (Cu) foils, two of which were used for InP growth and the other two were for Si growth. The preparation of the two InP growth samples consisted of one Cu foil with carbon deposition and the other without carbon deposition. A Cu foil was cleaned with acetic acid, rinsed with DI water, and dried in air. Subsequently, carbon deposition was conducted by annealing the Cu foil in hydrogen at 990 °C and 270 mTorr for 20 minutes followed by flow of methane/hydrogen mixture for 10 minutes, also at 990 °C and 270 mTorr. Following the carbon deposition, the Cu foil was allowed to cool in hydrogen, and then it was purged with argon before removal from the carbon deposition reactor. Another Cu foil was rinsed with acetone, isopropanol, methanol, rinsed in DI water, and dried in air. The two Cu foils, one with and the other without the carbon deposition, were further coated with Au colloidal nanoparticles with nominal diameters of 10 nm by drop casting and allowed to dry in air. Metal organic chemical vapor deposition (MOCVD) was used to deposit InP on the two Cu foils. The MOCVD growth conditions for InP were a growth time 20 minutes at 300 Torr, 550 C, and a 4.3 V/III molar flow rate ratio. The precursors were ditertiary butyl phosphine (DTBP) and trimethylindium (TMIn).

The preparation of the two Si growth samples also consisted of one Cu foil with carbon deposition and the other without carbon deposition. Two Cu foils were cleaned with acetic acid, rinsed with DI water, and dried in air. Subsequently, one Cu foil underwent the carbon deposition described earlier. Following the carbon deposition, the Cu foil was allowed to cool in hydrogen then purged with argon before removal from the reactor. The other Cu foil did not undergo the carbon deposition. The two Cu foils, one with the carbon deposition and the other without it, were coated with colloidal gold. Plasma enhanced chemical vapor deposition (PECVD) was utilized to deposit silicon. The PECVD for Si included a pre-growth annealing process performed at 400 °C for 5 min in hydrogen, which was followed by a nanowire growth step at growth temperature of 500 C. Disilane (Si_2H_6) hydrogen mixture was used as the silicon precursor and the flow rate was 10 sccm with a reactor pressure of 0.3 Torr and a growth time of 15 minutes. After the growth, the reaction chamber was evacuated and the sample was cooled to 50 °C in argon.

In summary, we have four samples in total in this experiment; InP with carbon on Cu, InP without carbon on Cu, Si with carbon on Cu, and Si without carbon on Cu. All four samples, InP on Cu foils with/without carbon deposition, and Si on Cu foils with/without carbon deposition, were characterized by various analytical tools including scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX), transmission electron microscopy (TEM), Raman spectroscopy, and x-ray diffraction (XRD).

3. Results and discussion

The Cu foils prepared with the carbon deposition were characterized prior to semiconductor (i.e., InP and Si) growth using Raman spectroscopy, in order to determine the nature of the grown carbon layer. Fig. 1 shows the Raman spectrum taken from the Cu foil that underwent the carbon deposition. Two peaks marked with “G” and “2D” are clearly seen and identified as two types of vibrational modes [21–23], suggesting the presence of graphene on the Cu foil. The “2D” mode appears to be sharper and more intense than the “G” mode indicating that the graphene is a single layer [24].

Fig. 2 investigates the InP growths using SEM. The SEM image shown in Fig. 2a, taken from the InP sample deposited on the Cu foil without carbon deposition, shows that a granular film was grown. The EDS confirmed that the grown film is composed of stoichiometric InP. While InP grew as films on Cu foils without a graphene intermediate layer, InP grew as nanowires only on the Cu foil with a graphene intermediate layer, as seen in Fig. 2b–d. Multiple nanowires appear to form from a central location in Fig. 2b. EDS indicates that their elemental composition consists of indium and phosphorus with a chemical composition approximately stoichiometric to InP. Fig. 2b demonstrates that a high density growth of InP nanowires can be grown on polycrystalline Cu foils by using a graphene intermediate layer. The image highlighted in Fig. 2c shows details of the rough surface morphology of the grown InP nanowires. A rough morphology of nanowires has been shown to reduce thermal conductivity, which is advantageous in thermoelectric applications [16]. The image shown in Fig. 2d depicts a nanowire at its early stage of development with an Au metallic cap at the tip.

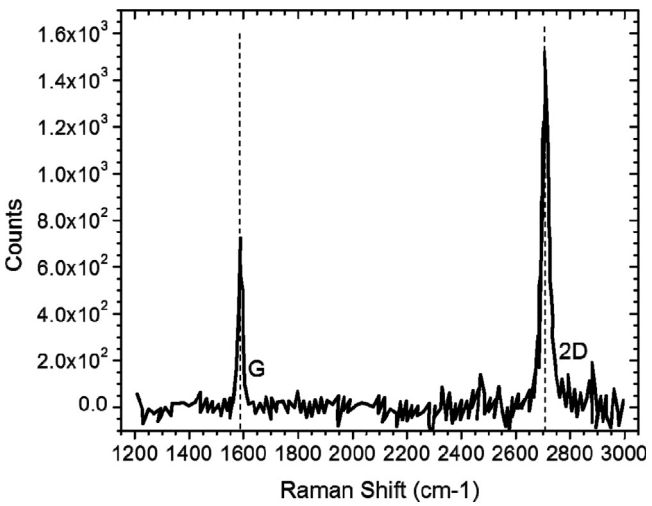

Fig. 1. Raman spectroscopy data taken on the carbon-treated copper substrate showing the distinct graphene peaks, G and 2D with the background PL signal removed.