Abstract—The unique properties of graphene are making it an attractive material for a wide variety of applications in nano-electronic. Various techniques have been developed to produce graphene to realize its potential applications. Chemical vapor deposition (CVD) of graphene films on Cu substrate is a primary technique for high quality graphene synthesis. In this work we demonstrate the growth of large area graphene layers by chemical vapor deposition (CVD) on copper substrates. Graphene growth was achieved by the flow of methane and hydrogen gasses over a copper thin film acting as catalyst at ambient pressure. Optimal growth conditions were found by varying the different parameters. A transfer process was carried out through treatment with a nickel etchant solution to isolate the graphene with using polymer bond for placement on an oxidized silicon substrate. Transfer methods are essential for effective optical contrast and SEM microscopy measurements. Characterization was performed with optical microscopy, Raman spectroscopy, XRD, SEM and other to determine the quality of layers.

Index Terms — Graphene, graphite, chemical vapor deposition, transferring, Raman spectroscopy.

I. INTRODUCTION

Graphene is one of the most interesting and promising novel materials in nanotechnology. Recently A.K Geim and K.S. Novoselov used a mechanical technique to peel graphene from graphite [1]. The great interest has developed in using graphene as nanoelectronic application due to its excellent physical and electrical properties such as tunable band gap, high thermal conductivity, and mechanical strength [2], [3]. It has exceptional carrier transport properties which makes it a promising material for future nanoelectronics [4]. Besides graphene’s high optical transmittance and conductivity it is also being considered as transparent electrode for flexible transparent displays and printable electronics [5]-[7]. To realize these potential applications, it is essential to synthesize high-quality and large-area graphene films. Chemical vapor deposition (CVD) of graphene films on Cu substrate is a primary technique for high quality graphene synthesis [8]-[10]. The metal substrate such as copper is put in to CVD furnace and heated under low vacuum to ~1000 OC for fabrication of graphene. Annealing carried out in hydrogen gas environment. Then methane and hydrogen gases are flowed in to quartz furnace. The hydrogen catalyzes a reaction between methane and surface of the metal surface causing carbone atoms from the methane gas to be deposited on to surface of copper through chemical absorption [11]. After process of deposition the furnace is quickly cooled to keep deposited carbon layer from aggregating into bulk, which formed into continuous or nonecontinuous graphene layers Fig. 1 a) and b). Different recipes have been proposed to obtain high quality graphene.

II. EXPERIMENTAL PROCEDURE

In this work we demonstrate the growth of large graphene layers by thermal chemical vapor deposition on copper substrates. In experiments polycrystalline Cu foil (Alpha
Aesar, 99.9999% metal basis) with thickness of 500 µm is used as a substrate. Then CH4 (20-40 sccm) as precursor gas is carried by H2 (20sccm:30 sccm) pressure is less than 5mTorr; and the graphene formation time is 20-40 min at ~1000 °C. After graphene formation, samples are cooled down by mechanically opening CVD box to decrease temperature in Ar (20sccm:40 sccm) atmosphere. Cooling rates are measured by a thermal couple on the sample holder. After graphene formation, samples are cooled down by mechanically opening CVD box to decrease temperature in Ar atmosphere Fig. 2 a). It is highly desirable to describe the underlying growing processes to optimize graphene growth conditions.

![Fig. 2. The growth of graphene layers by thermal chemical vapor deposition on copper substrates: a) photo of CVD heater during cooling process (CVD box open), on the top of photo is image of quartz tube during annealing process; b) schematic image of optimal CVD condition for fabrication large area graphene thin films.](image)

Cooling rates are measured by a thermal couple inside of the quartz tube. For transferring graphene to Si/SiO2 substrates, as-synthesized samples are coated by PMMA using a spinner. The spinning speeds are in range between 300 to 3000 rpm depending on the size of samples. After coating PMMA, samples are placed on an aqueous solution of Nickel Etchant for etching off the Cu substrate. Afterwards, graphene/PMMA films are scooped out from the solution, rinsed several times by DI water and placed on the Si/SiO2 substrates. At last, PMMA is removed by acetone.

After the film was transferred to SiO substrate, it was characterized by optical microscopy, Raman spectroscopy, and SEM. Besides we used carbon based structure like graphite oxide, graphene oxide and Highly Ordered Pyrolytic Graphite(HOPG) for comprising of Raman Spectra Optimal growth of graphene films were found by varying the different CVD conditions such as annealing temperature and gas flow rate. It was found that relatively uniform graphene formed at low gas pressure and fast cooling time for high purity Cu foils.

A. Characterization

The crystal structure and the chemical composition of obtained powders were analyzed by X-ray diffraction (Model D5005, Bruker, Karlsruhe, Germany) equipped with a primary graphite monochromatic selecting the Co Kα radiation. The voltage was 40 kV, and the current was 30 mA. The diffraction angle 2θ was chosen to be 30-90°. The scanning speed was 0.020 per 0.8 seconds. The microstructure of the specimens was investigated by FESEM (JSM-6500F, Japan) and the chemical content of iron and titanium of the specimens was evaluated by EDX. The effect of heat treatment on the mechanical properties of the composites was studied by measuring the hardness of the specimens before and after annealing. The hardness values of polished specimens were measured 10 times by Vickers's hardness test method, and average value was obtained for each sample [13]. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The corrosion resistance of the sintered STS: TiC₆N₅ specimens were evaluated by analyzing of the polarization curves. The testing electrolyte was 0.5M H₂SO₄ aqueous solution at 80 °C. The measurements were conducted using a measuring system Gamry-DC 105. The reference electrode was a saturated calomel electrode with carbon electrode as a support electrode. The measuring of potentiodynamic polarization current with a scan rate 1 mV/s was performed [13], [14].

III. RESULT AND DISCUSSION

The deposition technique of graphene should essentially provide precise control growing condition. In particular we suppose that deposition must terminated right after the several layers of graphene are formed on Cu substrate and then start fast cooling process for providing thin film uniformity. In other words in the chemical reaction is
controlled process, like the reaction rate of graphene deposition can be optimized by reaction temperature and concentration of the reactants. Hence it is helpful to reduce deposition temperature, increase cooling rate and decrease partial pressure during deposition on catalyst surface. However, temperature affects not only reaction process, but also to the microstructure of the substrate of the deposited film. The process of formation of grains with different size on copper surface after thermal annealing is shown in Fig. 3 a) and b). According this figure, before thermal annealing Cu surface have surface grooves caused by extrusion process Fig. 3 a) and grooves are disappeared after 1000 °C of thermal annealing. Instead of grooves on copper surface is formed different size of grains Fig. 3 b). We suppose that these grains have different growing plane of indexes [14]. That is why graphene was deposited in selective area of copper surface. Besides the key advantage to CVD growth is the ability to transfer the graphene to an arbitrary substrate. Ones graphene/copper foil cooled up to room temperature, after CVD treatment, a polymer material, such as polymethyl methacrylate (PMMA) can be coated on to graphene, then the copper removed using etchant, and PMMA can be removed in acetone. However in the SEM image of Fig. 3 it is shown that acetone cannot be totally removed from surface even after long time (~2 hours) of oxide treatment. The small fraction of polymer is left after acetone treatment, although it’s invisible in optical images Fig. 2 d). Therefore it is necessary to optimize of transferring processes or use direct transfer without polymer bonder.

Raman spectroscopy technique is optimal and most reliable method of determine the presence of graphene [15]. Graphene produced two strong optical peaks in Raman spectra: the G peak and the D peak. The G peak is due to individual bonds stretching and compressing, while D peak is due to formation modes of the hexagonal structures of carbon atoms. They occurs around 1300-1380 and 1550-1600 cm⁻¹, respectively. In particular, the different peak position of graphite oxide compared to graphene oxide and HOPG is shown in Fig. 4. Raman spectra shown in Fig. 4 a) display the G line at about 1570 cm⁻¹ and D line at 1340 cm⁻¹, respectively. The smaller peaks intensity ratio is assigned to graphitized structure and local defects particularly located subsurface areas. Raman spectra of highly oriented pyrolytic graphite Fig. 4 b) and CVD graphene films Fig. 4 c) transferred to SiO₂ are very similar to each other. The peaks around ~1580 cm⁻¹ are the G band which is inherent in graphite lattice; the peaks around ~ 2720 cm⁻¹ are attributed to the main 2D band in the subsurface region. The large surface area of graphene is thick and small defective because the D peak is appeared and the G peak is lower than 2D peak. According to the Raman spectra in most areas of surface graphene is multilayer [16].

![Fig. 3. SEM images of Cu surface before annealing (a) and graphene on copper foil after CVD treatment (b). Surface image of PMMA/graphene/SiO after acetone cleaning SEM image (c) and (d) optical microscope image. It is visible PMMA flecks on SiO₂ surface.](image)

IV. CONCLUSIONS

In this study large area graphene layers were grown by chemical vapor deposition on copper substrates. It was observed the process of formation of grains with different size on copper surface after thermal annealing. It is shown that that acetone cannot be totally removed from surface even after long time treatment. Probably it is necessary to use direct transfer of graphene on arbitrary substrate without using organic polymers. It was carry out comprision characteristic of Raman spectra of graphene, HOPG and graphite oxide. It is shown that Raman spectra of highly
oriented pyrolytic graphite and CVD graphene films transferred to SiO2 are very similar to each other. The peaks around ~1580 cm⁻¹ are the G band which is inherent in graphite lattice; the peaks around ~2720 cm⁻¹ are attributed to the main 2D band in the subsurface region.

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