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# 論　文　要　旨
# Thesis Abstract

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主論文題名　（Title） Fabrication of multilayer graphene by solid-phase reaction and application to gallium nitride based Schottky diodes


内容の要旨　（Abstract）

Now a days, global warming becomes one of the most focusing issue for the scientists and engineers all over the world. Global warming caused mainly due to the emission of greenhouse gases. A major part of energy used worldwide comes from fossil fuel combustion. To convert the fossil fuels to usable energy form greenhouse gas emissions are occurring and natural processes can absorb some of this emitted greenhouse gases while the rest of the emitted greenhouse gases are mainly responsible for the global warming. Therefore, to reduce the emission of greenhouse gases it is needed to reduce the energy consumption in society as well as industries to deduce the technological impact on greenhouse gas emission. For industrial aspect it is needed to fabricate high energy efficient and highly reliable devices to make the device environment friendly. The device fabrication temperatures should be reduced to decrease the energy consumption. Wide band-gap gallium nitride (GaN) and related materials are chemically stable compound semiconductors, and have attracted considerable interest for application in opto-electronic device and high power/high temperature electronic device. Devices made of nitride-based materials include metal-semiconductor-metal (MSM) ultraviolet (UV) light photo-detectors, metal semiconductor field-effect transistors (MESFETs), high electron mobility transistors (HEMTs), metal-oxide semiconductor field-effect transistors (MOSFETs), heterojunction bipolar transistors (HBTs) and Schottky rectifier diodes. For these applications, high quality Schottky contacts have been key factors in improving performance, reliability, and thermal stability.

Graphene/multilayer graphene (MLG) are being extensively studied for various applications such as narrow interconnects, an active or passive layer in electronic and optoelectronic semiconductor device and many more for its outstanding physical, electrical, optical, and mechanical properties and expected high thermal stability due to its high melting point. For the application of MLG as an interconnect material, improvement of crystallinity and uniformity at comparatively lower temperature is still a challenge. For the application of MLG to semiconductor devices (such as GaN power devices), transfer-free deposition is

better than those requires an additional transfer process. Several research groups reported on transfer-free deposition of MLG on n-GaN by thermal CVD. But, the deposition temperature is as high as 950 $^{o}$C and the MLG crystallinity is not good. Therefore, transfer-free deposition of MLG on n-GaN substrate with improved crystallinity and lowering the deposition temperature is required for most of the promising applications of MLG based n-GaN devices. This dissertation is concerned with the fabrication of MLG on $SiO_2$ and n-GaN substrates by solid-phase reaction (SPR) and application especially on n-GaN based Schottky diodes. MLG deposition by SPR has an advantage of transfer-free deposition on desired substrate. The improvement of crystallinity and uniformity are another challenge of our present work.

To improve the crystallinity of MLG on $SiO_2$ by SPR, a new approach of application of current stress during annealing of sputtered carbon doped cobalt (Co-C) layer was proposed. The Co layer acts as a catalyst for the SPR to occur. The effects of current stress on the formation and crystallinity of MLG films were investigated by comparing the characteristics of the films annealed at the same temperature with and without current by taking into account the temperature rise due to Joule heating. The characteristics obtained by Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) measurements revealed that the MLG films produced were crystalline in nature and their crystallinity increased with applied current stress at the same temperature. From SEM observations, beside Joule heating, reduction of nucleation sites of MLG induced by current stress may be the potential reason for the improvement of the crystallinity of MLG films. However, the MLG growth was not uniform over the entire substrate as was confirmed by SEM images. From the cross-sectional TEM image, it was found that the MLG growth took place at the sides of the Co. The non-uniform growth of MLG might be due to the growth originates from the crystalline facets. From the XRD measurements, Owing to the formation of new fcc phases of Co after applying current stress at the same temperature, it is easier for carbon atoms to form MLG at the fcc step site. Therefore, the predominance of fcc Co after applying current stress may be another reason for the improvement of MLG crystallinity. The uniformity of MLG films were improved by depositing an additional Cu capping layer over the Co-C layer. When a Cu capping layer is deposited over the Co-C layer, the Cu layer can suppress the agglomeration of Co, which leads to the uniform precipitation of MLG, since Cu does not form an alloy with Co at the annealing temperature used in our experiment.

The second approach of our present research was transfer-free deposition of MLG on n-GaN by SPR without extra catalyst by annealing sputtered a-C on n-GaN. Diamond like carbon films were found to form by annealing the a-C layer on n-GaN at temperatures between 800 and 1000 $^{o}C$. The surface uniformity of the samples were seen to be improved with the increase of annealing temperature. Crystallization of a-C occurred due to high temperature annealing or self catalization of Ga by breaking of GaN into Ga and $N_2$ at high temperature as was confirmed by XRD measurement. However, by this method the nanocarbon crystallinity was poor and the fabrication temperature was as high as 1000 $^{o}C$. For the reflection of performance of an MLG based device improvement of crystallinity of nano-carbon film similar to MLG are required. The lowering of the deposition temperature are required to reduce C diffusion to GaN.

To improve the crystallinity and uniformity of the MLG films on n-GaN by SPR an extra Co layer as catalyst was involved for SPR to occur. At first, MLG was deposited by annealing room temperature (RT)-sputtered Co/C layer on n-GaN. The characterization made by Raman spectroscopy, it was found that the graphitization stopped after annealing the structure at 750 °C. From the XRD measurement of RT sputtered and annealed Co/C layer, it was found that the reaction between Co and GaN took place and a $Co_2O_3$ phase appeared after annealing at 750 °C, that might be responsible for non-graphitization. Also from the SEM images of the RT-sputtered and annealed film, it was found that the surface of the MLG films were not uniform over the entire substrate. The non-uniformity was considered due to the difference in thermal expansion between GaN and the sputtered films. The MLG crystallinity and uniformity were improved significantly after applying heat sputtering for the deposition of amorphous C and Co layers in comparison that with conventional RT sputtering. The growth conditions for MLG with improved crystallinity and uniformity were optimized as follows: 150 $^{o}C$ sputtering of the Co/C layers annealed at 650 $^{o}C$. Decreasing the difference in the thermal expansion between GaN and Co/C, the suppression of the reaction between GaN and Co, and by cleaning of the GaN surface before sputtering might be the reasons for the improvement in the crystallinity and uniformity. This method of MLG fabrication will be promised with further success in fabricating an MLG based GaN device. Our next approach was to fabricate a device with MLG deposited by our proposed method.

The fabrication of an MLG based device with transfer-free deposition of MLG on n-GaN by SPR has been demonstrated by our proposed method. The MLG/n-GaN Schottky barrier diodes (SBD) were fabricated with transfer-free deposition of MLG on n-GaN by SPR. The as-deposited MLG/n-GaN diode showed rectification with a barrier height of 0.72 eV. For the as-deposited diodes, Schottky barrier height (SBH) was found to be in good agreement with other available reported values. The thermal stability of the diodes were measured by measuring the I-V characteristics after annealing the diodes without annealing and after annealed at various temperatures ranging from 200 to 500 °C in vacuum of $5 \times 10^{-}$

$^{3}$ Pa and was compared with a conventional Ni/n-GaN diode. It was found that the MLG/n-GaN diodes showed better thermal stability with more stable SBH than a conventional Ni/n-GaN diode annealing up to 500 °C. The diode properties calculated by TE model and Cheung's method was found to be in good agreement with one another. The unaffected interface reaction with annealing and the prevention of Au diffusion to n-GaN due to action of MLG as Au diffusion barrier layer was confirmed by XRD measurement is considered to be the reason behind the thermal stability. However, the series resistance of MLG/n-GaN diode was found to be higher than the Ni/n-GaN diode. Reduction of series resistance will be necessary for promising application of our MLG/n-GaN SBD with MLG deposited by our proposed method.

To reduce the series resistance of fabricated MLG/n-GaN diode, the top contact metal was changed from Au to Cu, since, the resistivity of Cu is lower than Au. Upon changing the top metal, there was no significant reduction in series resistance, therefore, the series resistance of our fabricated device is predominated by MLG layer. Our next approach is to decrease the MLG thickness as small as possible. This work is currently underway.

Finally, achievements of this dissertation are as follows: 1) Improvement of MLG crystallinity on dielectric substrate at comparatively lower temperature by SPR, 2) Uniform deposition of MLG on $SiO_2$ substrate with additional Cu layer as capping on Co-C layer, 3) Transfer-free deposition of MLG on n-GaN for the first time by SPR with improved crystallinity and uniformity at comparatively lower temperature, 4) Fabrication of an MLG/n-GaN Schottky barrier diode with higher thermal stability than a Ni/n-GaN Schottky diode with transfer-free deposition of MLG by our new method. With further improvement, our method will be promising for low resistance interconnect and improved thermal stability of n-GaN Schottky diodes.

The implementation of our new proposed method of MLG fabrication on $SiO_2$ substrate will lead to fabricate a low resistance narrow interconnect. MLG fabrication on n-GaN by our proposed method will lead to fabricate a wide-band gap semiconductor power device (n-GaN) with thermally stable Schottky contact that can be driven at high frequency and high temperature, and downsizing of the device. By replacing conventional Si power device with GaN power device, energy saving is anticipated. The fabrication temperature is lowered that will also reduce the energy consumption from the conventional energy sources during fabrication and will reduce the emission of greenhouse gases responsible for global warming.