Invited Paper

Large Area Low Temperature Ultrananocrystalline Diamond (UNCD) Films and Integration with CMOS Devices for Monolithically Integrated Diamond MEMS/NEMS-CMOS Systems

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ABSTRACT

Because of exceptional mechanical, chemical, and tribological properties, diamond has a great potential to be used as a material for the development of high-performance MEMS and NEMS such as resonators and switches compatible with harsh environments, which involve mechanical motion and intermittent contact. Integration of such MEMS/NEMS devices with complementary metal oxide semiconductor (CMOS) microelectronics will provide a unique platform for CMOS-driven commercial MEMS/NEMS. The main hurdle to achieve diamond-CMOS integration is the relatively high substrate temperatures (600-800 ^{o}C) required for depositing conventional diamond thin films, which are well above the CMOS operating thermal budget (400 ˚C). Additionally, a materials integration strategy has to be developed to enable diamond-CMOS integration. Ultrananocrystalline diamond (UNCD), a novel material developed in thin film form at Argonne, is currently the only microwave plasma chemical vapor deposition (MPCVD) grown diamond film that can be grown at 400 ˚C, and still retain exceptional mechanical, chemical, and tribological properties comparable to that of single crystal diamond. We have developed a process based on MPCVD to synthesize UNCD films on up to 200 mm in diameter CMOS wafers, which will open new avenues for the fabrication of monolithically integrated CMOS-driven MEMS/NEMS based on UNCD. UNCD films were grown successfully on individual Si-based CMOS chips and on 200 mm CMOS wafers at 400 ˚C in a MPCVD system, using Ar-rich/CH_4 gas mixture. The CMOS devices on the wafers were characterized before and after UNCD deposition. All devices were performing to specifications with very small degradation after UNCD deposition and processing. A threshold voltage degradation in the range of 0.08-0.44V and transconductance degradation in the range of 1.5-9% were observed.

Keywords: Ultrananocrystalline diamond films, large area deposition, low temperature, integration with CMOS devices, MEMS/NEMS devices.

1. INTRODUCTION

The ultrananocrystalline diamond (UNCD) films developed and patented by our group at Argonne National Laboratory exhibit high hardness and Young modulus, [1] chemical inertness, high electrical conductivity when doped with nitrogen, [2] negligible force of adhesion (stiction), [3,4] and biocompatibility, all properties that make UNCD an outstanding material for application to high-performance, harsh environment-compatible MEMS/NEMS devices, such as resonators and switches, [5] biomedical devices, and biosensors. In this respect, recent work by our group at ANL has demonstrated fabrication of functional RF-MEMS switches and resonators based on UNCD [5]., Transition of this

Micro- and Nanotechnology Sensors, Systems, and Applications, edited by Thomas George, M. Saif Islam, Achyut K. Dutta,
Proc. of SPIE Vol. 7318, 731817 · © 2009 SPIE · CCC code: 0277-786X/09/$18 · doi: 10.1117/12.822794

technology to the industry, however, will depend critically on the ability to produce UNCD films on large area wafers with thickness (≤ 5%) and microstructure uniformity compatible with large-scale device manufacturing. Recent work in our group at Argonne resulted in 4%, 6%, and 11% uniformity in UNCD film thickness across 100 mm, 150 mm, and 200 mm diameter Si substrates, respectively, using 2.45 GHz (for UNCD growth on 100 mm wafers) and 915 MHz (for UNCD growth on 150 and 200 mm wafers) microwave plasma chemical vapor deposition (MPCVD) process. All the films were grown either at 400 or 800 ^{o}C. The work reported in this paper includes a description of systematic measurements of film thickness, microstructure uniformity, and bonding configuration of UNCD films, using atomic force microscopy (AFM), Raman spectroscopy, and X-ray absorption near edge spectroscopy (XANES) techniques, respectively. In addition to UNCD film uniformity on large area wafers, it is important to develop a synthesis process, which would enable the integration of UNCD films with CMOS devices in order to provide the basis for the production of a new generation of monolithically integrated diamond MEMS/NEMS/CMOS devices for low power CMOS driven MEMS/NEMS –based systems. In this respect, our group at Argonne has also demonstrated that the UNCD film synthesis process provides a unique means of producing diamond films at ≤ 400 ˚C[6] with device fabrication-compatible growth rates (0.3-0.4 µm/hr) and synthesis temperature compatible with the CMOS thermal budget. This paper provides a discussion of our recent advances on the important scientific and technological topics described above.

2. EXPERIMENTAL METHOD

The large-area UNCD films discussed in this paper were produced in a new 915 MHz MPCVD system recently installed in the clean room of the Center for Nanoscale Materials at Argonne National Laboratory. The DiamoTek 1800 series 915 MHz, 10 KW MPCVD system from Lambda Technologies uses patented tunable cavity design to ensure optimum mode control for plasma generation and coupling efficiency. The microwave coupling system is designed to provide the necessary flexibility ("tunability") to facilitate efficient energy transfer for a wide range of processes. This includes the ability to position the plasma height with respect to the substrate and change the shape of the plasma (donut vs. spherical), which greatly helps to achieve thickness uniformity of UNCD films on substrates with up to 200 mm in diameter. The plasma is confined in an optically transparent quartz bell jar (diameter = 18"), which facilitates the probing of plasma chemistries by an optical fiber for optical emission spectroscopy. The plasma confined in the bell jar does not touch the walls at any time due to the bell's wide size (18" diameter) and therefore the risk of film contamination due to plasma etching of the quartz wall is considerably low or negligible. The custom-built substrate heater stage is a two-zone resistive heater with ability to independently heat each zone (inner or outer) to compensate for additional heating due to the plasma shape. The whole heater assembly is encased in an inconel shell and isolated from the plasma. In addition, the heater stage is differentially pumped separately to minimize contaminations originating from heating components in the heater stage. The system is fully automated, computer-driven operation, starting from loading of a wafer, deposition of diamond films with specific growth recipe to final unloading after deposition. The system can be controlled remotely via web interface and therefore offers greater flexibility for day-to-day operations. Fig. 1 shows the photograph of MPCVD system in operation at the ANL-CNM clean room.

Prior to UNCD deposition, the surface of the substrate needs to be seeded with diamond nanoparticles or even diamond microparticles to initiate the nucleation of UNCD. The seeding is currently done either via dry polishing of the substrate surface with polishing clothes embedded with diamond particles or by ultrasonicating the substrate in a solution containing a suspension of the diamond for an appropriate period of time. The UNCD film uniformity depends critically on the seeding step, particularly for growing at lower substrate temperatures, since growth kinetics is considerably sluggish at lower substrate temperatures due to retarded surface diffusion process, which affects directly the initial incubation time period required for the stabilization of diamond nuclei on non-diamond substrates. We have developed a substrate preparation and seeding process specifically for UNCD synthesis at low temperatures (~ 400 ˚C). It consists of depositing a thin (10 nm) layer of tungsten (W) film on the surface of Si substrates, for example, and then ultrasonic seeding using nanodiamond suspension in Dimethylsulphoxide (DMSO) solution diluted with methanol. This process disperses nanodiamond particles uniformly on the substrate surface with minimum agglomeration and provides very high initial nucleation density. Additionally, the tungsten interlayer forms carbide at very early stages of diamond growth due to very low diffusion coefficient of carbon (10^{-13} cm^2 $.s^{-1}$) in tungsten resulting in reduced initial incubation time for diamond nucleation [7]. Thus, uniform UNCD films can be grown using this process with surface roughness almost of the order of the grain size (4-6 nm).

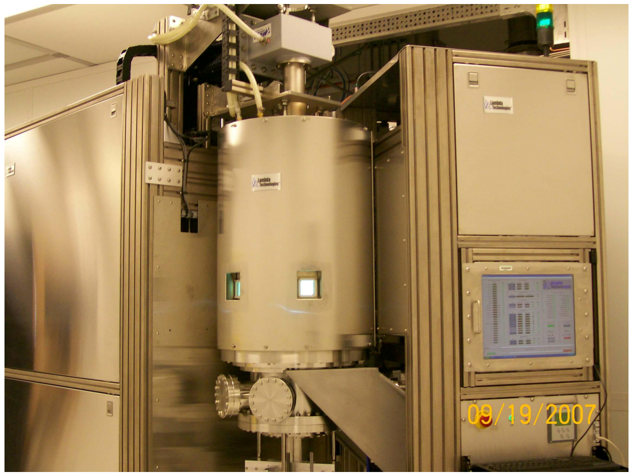
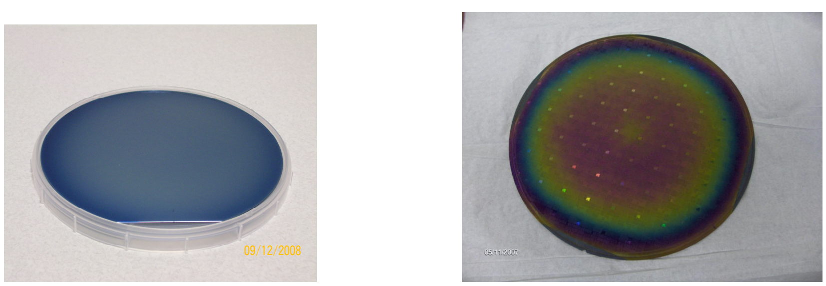


Figure 1. 915 MHz large area MPCVD system in operation in the clean room at the Center for Nanoscale Materials, ANL.

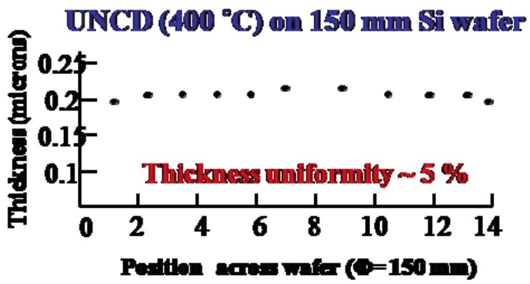
3. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show photographs of low temperature UNCD thin films grown on 150 mm in diameter bare Si wafer and 200 mm in diameter Si-CMOS wafer, respectively. Figures 3(a) and 3(b) show the thickness uniformity across the 150 mm bare Si and 200 mm CMOS wafers corresponding to Figs. 2(a) and 2(b), respectively. In both cases, UNCD films were grown using conventional Ar/CH_4 gas chemistry with some added percentage of H_2 (~3%). As shown in Fig. 3, the thickness uniformity measured on these wafers by using Filmetrix interferometric technique, and verified using SEM cross-section, is around 5% for 150 mm diameter wafers and 10-11% for the 200 mm diameter wafer, which is unmatched with any other MPCVD technique.

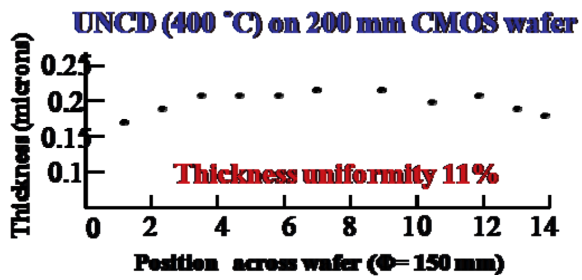


(a) (b)

Figure 2. Photographs of (a) 150 mm diameter Si wafer and (b) 200 mm diameter Si-CMOS wafer with UNCD thin films grown at 400 ^{o}C.

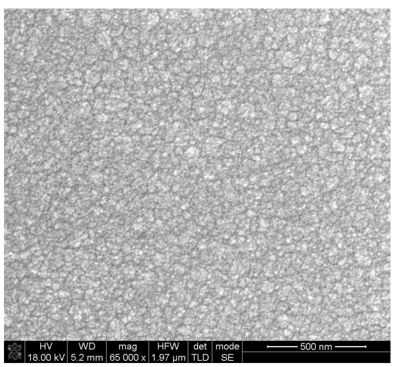


(a)

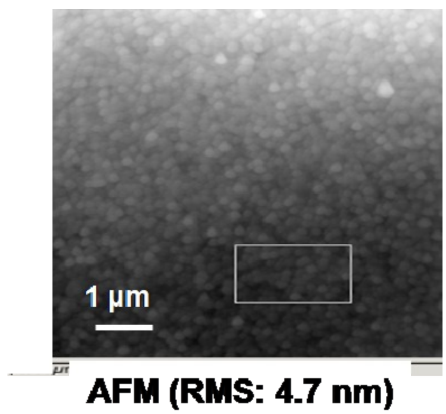


(b)

Figure 3. (a) Thickness across the 400 ˚C UNCD film grown on the 150 mm bare Si wafer shown in Fig. 2 (a); (b) thickness across the 400 ˚C UNCD film grown on the 200 mm Si-CMOS wafer shown in Fig. 2 (b).



(a)



(b)

Figure 4. (a) SEM image and (b) AFM micrograph of a 400 ˚C UNCD thin film. The AFM measurement shows a surface roughness of about 5 nm rms.

The surface morphology, roughness, and chemical bonding configuration of the UNCD films were characterized using SEM, and AFM analysis, and Raman and NEXAFS spectroscopies, respectively. Figure 4 shows SEM (a) and AFM (b) images of 400 ˚C UNCD film grown on a Si substrate. The SEM and AFM images show the typical surface morphology of a UNCD film.

The Raman measurement (He-Ne laser wavelength 632.8 nm) and NEXAFS measurement taken on the same UNCD film is shown in Figures 5(a) and 5(b), respectively. Raman spectra were taken from 3 different parts of the wafer (edge, center and in between) and do not show any significant variation indicating good phase uniformity of the UNCD film on a 150 mm diameter wafer. Raman measurements do not show a sharp peak at 1332 cm^{-1} wave number characteristic of sp^3 diamond but rather, small hump around 1340 cm^{-1}due to very small grain size of UNCD grains (2-5 nm). On the other hand, the relatively high intensity peak at 1580 cm^{-1} is indicative of sp^2 bonded carbon. This is due to the smaller grain size of UNCD (2–5 nm) and the high volume fraction of grain boundaries. These grain boundaries are only a few atoms wide and are composed of a mixture of sp^3 and sp^2-bonded carbon. The visible Raman spectrum of UNCD is thus dominated by scattering from the sp^2-bonded carbon located at the grain boundaries [2]. NEXAFS is particularly useful for probing the local bonding configuration in nanostructured carbon materials. Unlike Raman spectroscopy, it is equally sensitive to sp^3- and sp^2-bonded carbon. Since NEXAFS probes the core-hole-perturbed local density of unoccupied states in the near-surface region of a sample, the spectra obtained from diamond and graphite are very different due to the distinct structures of their unoccupied electronic states, and sp^3 and sp^2 percentages can be determined from the spectra. [3,4]

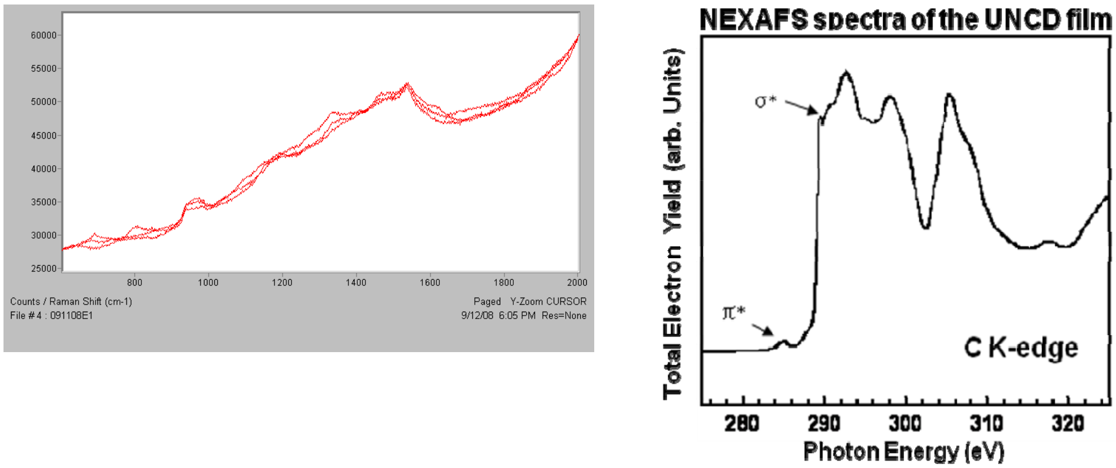
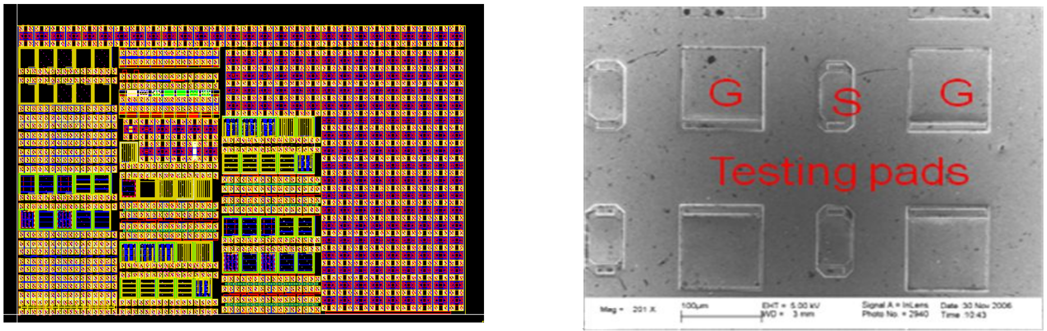


Figure 5. (a) Raman spectra (wavelength: 632.8 nm) of a 400 ˚C UNCD film and (b) NEXAFS spectra of a UNCD film taken at C 1s absorption edge.

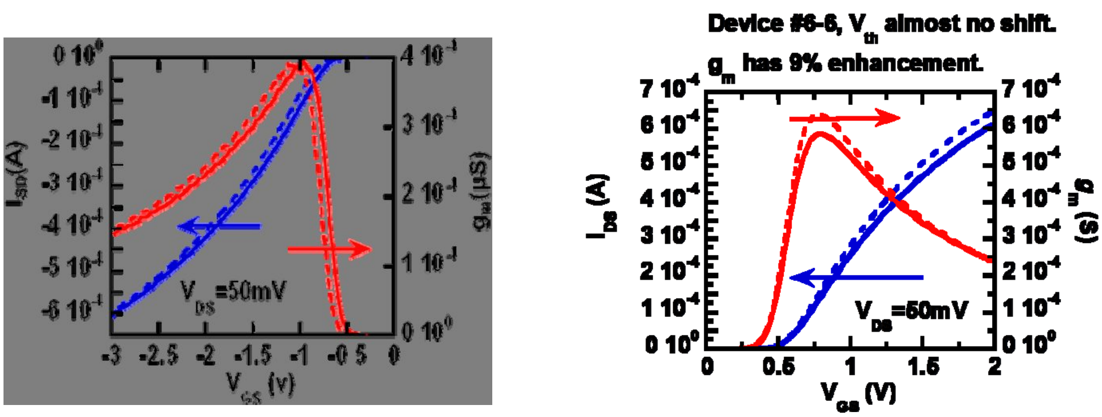
The NEXAFS spectrum from the UNCD film (Fig. 5b) exhibits distinct and well-known spectral features associated with crystalline sp^3 bonding including the diamond exciton at 289.3 eV, and the C 1s→σ* transitions at 289.3 eV, which include the second bandgap of diamond that produces a pronounced dip at 302 eV. The diamond exciton peak at 289.3 eV is slightly broader and somewhat diminished in intensity compared to the very sharp exciton peak observed for single-crystal diamond, due to the confinement of the exciton in the nanocrystalline grains. A small peak associated with sp^2 bonding at 285 eV is due to the C 1s→π* transition and comes from the sp^2- bonded carbon at the grain boundaries. The calculated sp^2 fraction was found to be 2.6%, which is slightly lower than the 5% sp^2 content identified in previous NEXAFS studies. All the characterizations studies carried out on the low temperature UNCD films grown on si substrates have demonstrated that the deposited UNCD film is of high quality and not any different from that of deposited at higher temperature. The same growth recipe were used for UNCD films grown on CMOS-chips and CMOS wafers.

In order to study the effect of UNCD deposition on CMOS functionality, individual CMOS on Si chips (from United Microelectronics Corporation, Taiwan) and CMOS wafers (from FreeScale Semicondictor) were coated with low temperature (400 ˚C) UNCD films. NMOS and PMOS devices from different parts of the CMOS wafers were tested for any change in their electrical characteristics. Prior to UNCD deposition, 1-micron thick SiO_2 film was deposited on the CMOS wafer using a PECVD process to electrically isolate CMOS testing pads. A tungsten layer (thickness: 10 nm) was then sputter coated on top of the SiO_2 layer as a seed layer for UNCD deposition, which is then seeded using nanodiamond suspension as previously described, and then subjected to UNCD deposition process. After UNCD deposition, the films were characterized using Raman and NEXAFS spectroscopy, which confirmed that the UNCD films grown on a tungsten layer are essentially same as those grown on Si substrates. The access to testing pads on the CMOS wafer, was then achieved by series of fabrication steps, including photolithography to define pad areas, etching of diamond using oxygen RIE, wet etching of tungsten interlayer, and dry etching of the SiO_2 layer using RIE. I-V characteristics of the PMOS and NMOS were measured using probe station and individual devices from various regions on the wafer were examined for change in gate threshold voltage and transconductance to test for any shift as a result of UNCD deposition and other fabrication processing. Figures 6(a) and 6(b) show a photograph of Si-CMOS devices and a SEM picture of the CMOS devices coated with a 400 ˚C UNCD films, respectively. Figures 7(a) and 7(b) show the results of electrical measurements carried out on the CMOS wafer, before and after UNCD deposition. Fig. 7(a) shows slight increase in the gate threshold voltage (V_{th}) by 0.08 V and slight decrease in transconductance by 1.5% on PMOS devices, whereas Fig. 7(b) shows slight increase in gate threshold voltage(V_{th}) by 0.03 V and some increase in transconductance by 9% in a NMOS device. All these variations in threshold voltages and in transconductance are well within the limit and sufficient to drive any integrated MEMS device on chip with CMOS. This clearly demonstrates that UNCD deposition and processing steps did not affect adversely the CMOS functionality and it is possible to fabricate UNCD MEMS devices on CMOS where UNCD MEMS devices could be drive by on-chip CMOS.



(a) (b)

Figure. 6 (a) Layout of a CMOS on Si microchip and (b) SEM image of the same chip after UNCD deposition.



(a) (b)

Figure 7: Transfer characteristics (to extract gate threshold voltage, V_{th}) and transconductance (g_m) curves obtained on (a)PMOS and (b) NMOS devices before (solid lines) and after (dashed lines) UNCD deposition at 400 ˚C.

Thus, the data presented in Figures 6 and 7 clearly demonstrate that the low temperature UNCD growth process including processing steps are compatible with CMOS thermal budget and UNCD based MEMS/NEMS could be directly integrated with CMOS electronics. This opens the pathway to a new generation of monolithically integrated diamond-MEMS/NEMS/CMOS devices.

4. SUMMARY

In summary, we have demonstrated a process based on 915 MHz MPCVD to grow highly uniform UNCD thin films on large area substrates (150-200 mm diameter) with manufacturing-compatible thickness uniformity, a necessary condition to develop UNCD based MEMS devices with reasonable yield for commercialization. We further demonstrate that our process is compatible with CMOS by growing UNCD films on CMOS wafers and measuring the electrical parameters of the devices on the CMOS after UNCD deposition. All devices were performing to specifications with acceptable degradation after UNCD deposition and processing. A threshold voltage degradation in the range of 0.08-0.44V and transconductance degradation in the range of 1.5-9% were observed. We believe that this achievement opens the pathway for the development of a new generation of monolithically integrated diamond-MEMS/NEMS/CMOS devices that may have a major impact on the commercialization of systems based on this technology.

5. ACKNOWLEDGEMENT

This work was supported by DARPA under contract MIPR06-W238 and the use of the Center for Nanoscale Materials was supported by the US Department of Energy, BES-Materials Sciences, under contract DE-AC02-06CH11357. One of the author AVS would like to thank Mr. Andrew Konicek from University of Pennsylvania for the NEXAFS measurements on the UNCD sample.

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