

SURFACE MODIFICATION OF CHEMICAL VAPOR DEPOSITION (CVD) DIAMOND /SILICON FILM(111) BY IMPLANTATION WITH FE + B IONS AND THEIR MAGNETIC PROPERTIES

MODIFIKASI PERMUKAAN FILM CVD INTAN/SILIKON(111) DENGAN IMPLANTASI ION FE + B DAN SIFAT MAGNETIK BAHAN

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ABSTRACT

SURFACE MODIFICATION OF CHEMICAL VAPOR DEPOSITION (CVD) DIAMOND/SI(111) FILM BY IMPLANTATION WITH Fe+B IONS AND THEIR MAGNETIC PROPERTIES. Surface modification of CVD manufactured diamond films on Si(111) substrate has been performed by means of Fe+B ion implantation followed by Argon ion gas sputtering with acceleration energy 20 keV and ion dose 1×10^{15} and 1×10^{16} ions cm^{-2} . Scanning Transmission Electron Microscope (STEM) imaging shows the formation of amorphous carbon layer on top of the diamond film with thickness ca. 100 nm on the implanted sample and ca. 20 nm on the sample without implantation. The morphology and magnetic property of the films surface were characterized by Atomic and Magnetic Force Microscopy (AFM/MFM). The Electron Energy Loss Spectroscopy EELS analysis has revealed amount of Boron atoms distributed homogenously inside the carbon amorphous layer on both samples which is in close agreement to the result of Raman Spectroscopy showing the changes of the Raman spectrum due to implantation. The magnetic properties of the samples after Fe+B ion implantation were additionally investigated by means of Vibrating Sample Magnetometer (VSM). By increasing ion doses at constant energy 20 keV, the magnetoresistance property decreased from +45% on the sample implanted with dose 1×10^{15} to +8% on the sample implanted with dose 1×10^{16} ions cm^{-2} .

Keywords: CVD Diamond film, ion implantation, magnetoresistance, nanostructure

ABSTRAK

MODIFIKASI PERMUKAAN FILM CVD INTAN/SI(111) DENGAN IMPLANTASI ION Fe + B DAN SIFAT MAGNETIK BAHAN. Modifikasi permukaan film CVD (Chemical Vapor Deposition) dengan substrat Si(111) telah dilakukan dengan teknik implantasi ion Fe + B yang diikuti dengan proses sputtering ion gas Argon pada akselerasi energi 20 keV pada dosis ion 1×10^{15} and 1×10^{16} cm^{-2} . Citra STEM (Scanning Transmission Electron Microscope) memperlihatkan adanya pembentukan lapisan Karbon amorf pada lapisan paling atas dari film Intan dengan ketebalan kurang lebih 100 nm untuk cuplikan yang terimplantasi dan tebal 20 nm untuk cuplikan yang tidak terimplantasi. Morfologi dan sifat magnetik permukaan film dikarakterisasi dengan AFM/MFM (Atomic dan Magnetic Force Microscopy). Hasil analisis dengan teknik EELS (Electron Energy Loss Spectroscopy) memperlihatkan keberadaan atom Boron yang tersebar secara merata di dalam lapisan amorf Karbon dan hal ini bersesuaian dengan citra spektroskopi Raman untuk kedua cuplikan. Sifat magnetik film dapat teramati dengan VSM (Vibrating Sample Magnetometer), sedangkan sifat magnetoresistance bahan diukur dengan teknik Four point probe. Diperoleh hasil bahwa seiring dengan meningkatnya dosis ion pada energi tetap 20 keV, nisbah magnetoresistance berkurang dari positif 45% pada sampel terimplantasi dengan dosis 1×10^{15} menjadi 8% pada sampel terimplantasi dengan dosis 1×10^{16} ion cm^{-2} .

Kata kunci: Film CVD intan, implantasi ion, magnetoresistance, struktur nano

INTRODUCTION

Diamonds naturally are strong diamagnetic. However, their ferromagnetic property can be enhanced either by ion implantation which is directly correlated to the defects formation or by addition of atom size impurities. Talapatra et al. [1] found ferromagnetism (FM) in nanosize diamond crystals as a result of nitrogen and carbon ion implantation. This finding opens the possibility of using diamond for many electronic applications such as nano size magnetometry [2]. SRIM [3] has revealed that the defect density threshold by boron ion, beyond which graphitization occurs during annealing is as high as 10^{22} vacancies/cm³. Tavares et al. [4] were develop p-type diamond single crystal layer on (111) oriented diamond substrates grown by Microwave Plasma-enhanced Vapor Deposition (MPCVD). Hohne et al. [5] studied the boron, fluorine or iron implantation on the diamond film to produce structures with different degrees of lattice damage and their magnetic properties. On the other hand, Y.J. Fei et al. [6] obtained longitudinal resistance change rate is up to +20% at 20 Tesla and temperature 300 K at post implanted boron with dose 3×10^{19} ions cm⁻². Unfortunately, there are no information about any research works which investigate the role of implantation with low doses ions Fe+B on the surface of CVD diamond/Si(111).

In this present work, the ion beam irradiation was applied with the aim to modify the structure of CVD manufactured diamond film on Silicon(111) substrate in order to increase the magnetic property. At first step Fe+B ions of various doses but at constant acceleration energy 20 keV have been deposited on the diamond film surface followed by Argon ion sputtering at 70 keV and dose 10^{16} ion cm⁻². The direction oriented Si(111) substrate was used to keep the diamond structure of the film even after ion implantation. We postulate that ion implantation of certain atoms such as Fe or B, or their combination and subsequent ion sputtering by Argon could bring the positive effect to the magnetic properties of diamond film which give rise to the magnetoresistance property at low magnetic field.

METHODOLOGY

CVD diamond film of 1300 nm thickness on Silicon wafer (111) used in this work was manufactured and supplied by Applied Diamond Inc. USA. Two samples of such diamond films were implanted by Fe+B ion at energy 20 keV with ion doses 1×10^{15} (thereafter called B-E1D1) and 1×10^{16} ion cm⁻² (called as B-E1D2) followed by Argon ion sputtering at 70 keV and dose 10^{16} ions cm⁻². Phase identification of the film was performed using Raman Spectroscopy. The magnetization measurements were carried out using an Oxford VSM. The samples were cut from the bulk with area of about 4 mm². The characteristic hysteresis loop was measured between +1 and -1 Tesla at room temperature. The magnetoresistance measurements were carried out by Four Point Probe technique at magnetic field up to 0.8 Tesla at room temperature. All the measurements were taken at PSTBM-BATAN. Implantation process was performed by Ion Implanter at PSTA-BATAN in Jogjakarta. The microstructure of the film was characterized by TEM FEI Tecnai G2 with acceleration energy 200 keV equipped with EELS and Energy Filter at the Central Facility for Electron Microscopy at RWTH Aachen University of Technology, Germany. All the samples for TEM investigation were prepared in the Focus Ion Beam workstation (FIB) FEI Strata 205. The detail description about the FIB preparation technique has been reported in [7]. Additionally the surface morphology and the magnetic properties of the film surface were investigated by AFM and MFM at RWTH Aachen, Germany.

RESULTS AND DISCUSSION

Depth Distribution Simulation

SRIM computer code [3] was used to simulate the in depth distributions of the implanted ions in the CVD diamond samples. As shown in Figure 1a, the Fe ions were implanted in the diamond film surface down to 16.7 nm depth, thus almost on the top most film surface. While Boron was distributed in the film surface deeper up to 55.0 nm, Figure 1b. The Fe ions density is 7×10^5 atom cm⁻², while boron ions' is 2.4×10^5 atom cm⁻².

The Iron (Fe) ions were implanted into diamond film until at range 167 Angstrom (16.7 nm), almost on the top film surface. While Boron (B) was entered the film more deep until range 580 Angstrom (58.0 nm) due to the

ions mass of Boron lower than the ion mass of Iron as shown in Figure 1. Density of Iron (Fe) ions are 7×10^5 atom cm^{-2} , while Boron ion's is 2.4×10^5 atom cm^{-2} .

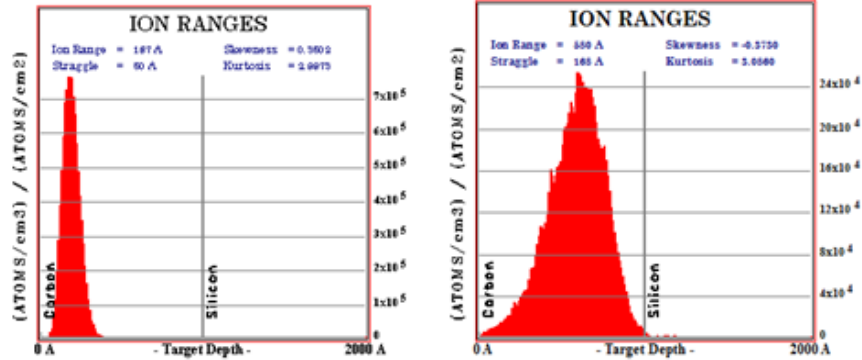


Figure 1. Calculated iron (Fe) ion depth profile (left) and boron (B) ion depth profile (right) implanted into CVD diamond film by SRIM code.

Morphology Surface Film

The surface morphology of B-E1D1 samples was measured by AFM. The result is shown in Figure 2a. While its magnetic property was measured by MFM, Figure 2b. The surface morphology of sample B-E1D1 shows typical diamond structure. The maximum height of the diamond tip is about 125 nm. MFM view somehow shows magnetic contrast at the same pattern as the AFM result. The distribution of this pattern has maximum height at 107.8 nm. However, the film surface seems to be smoother in magnetic contrast. This might be related to the existence of Fe ion on the top of surface film as described by SRIM simulation.

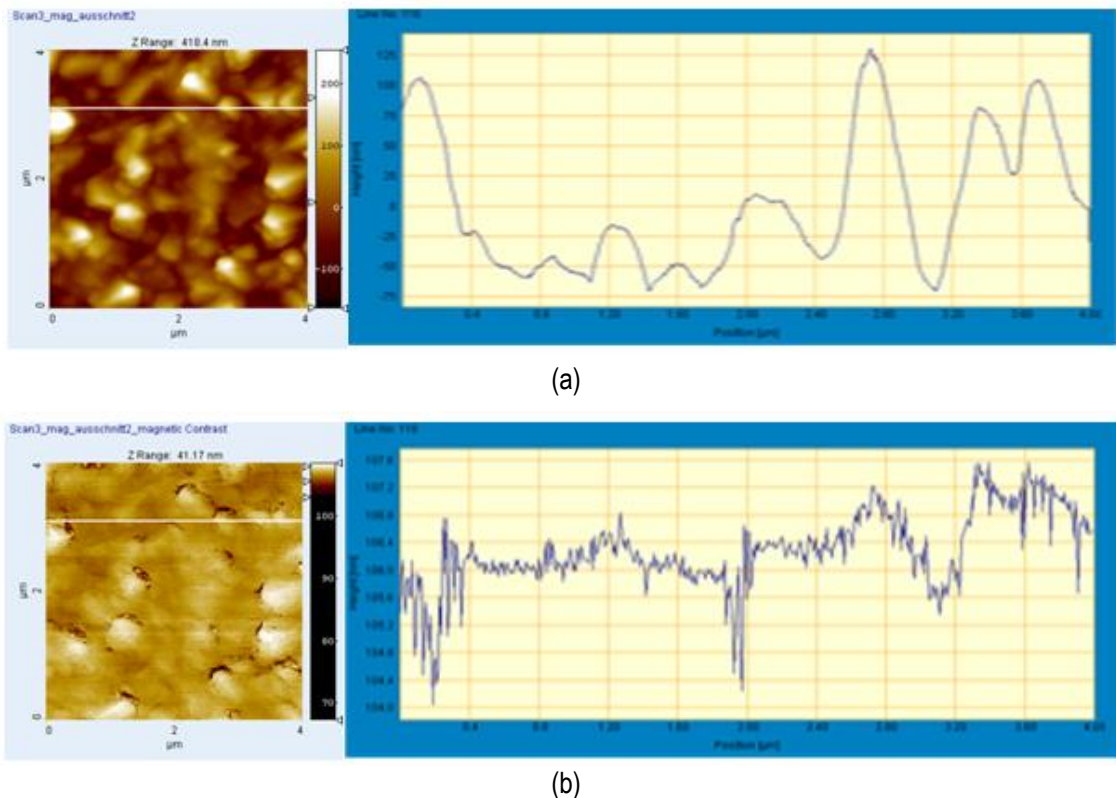


Figure 2. Surface morphology of samples B-E1D1 seen by AFM (a) and by MFM (b)

Microstructure Properties (TEM-EELS)

Figure 3a shows a typical TEM image in scan mode recorded by High Angel Angular Dark Field (HAADF) detector of CVD diamond film cross section after Fe+B ion implantation at dose 1×10^{15} ions cm^{-2} with the total film thickness ca. 1000 nm. One can observe the amorphous layer of 100 nm thickness on the top of the columnar poly crystal diamond film. The image in Figure 3b was acquired using Energy Filter on the EELS boron edge showing the presence of Boron atoms distributed relative homogenously in the amorphous layer.

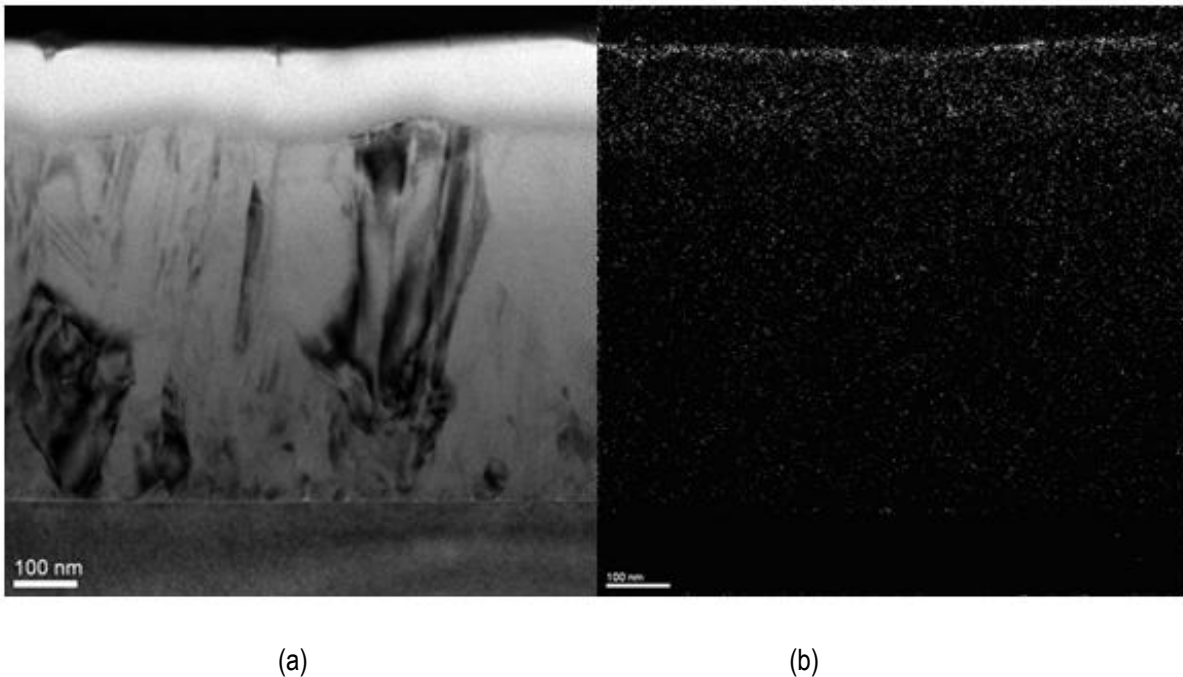


Figure 3(a). Left side was a typical of TEM image of CVD diamond film B-E1D1 sample with amorphous diamond around 100 nm at the top layer

Figure 3(b). Right side were boron atom and amorphous diamond distribution image at the top layer and carbon at the middle of the sample taken by EELS

Raman Spectroscopy

In order to study the surface condition the Raman spectroscopy measurement at laser energy of 25 mW is used, because this technique is sensitive to the presence of light element such as Carbon atom. From Raman spectrum in Fig. 4 is obvious, a modification of the diamond surface in the range $1000\text{-}1600\text{ cm}^{-1}$ on both samples. The low dose B-E1D1 sample shows strong Raman peak characteristic for diamond at wave number of 1325 cm^{-1} , while graphite peak is not visible at wave number around 1580 cm^{-1} . At high dose of 1×10^{16} ions cm^{-2} B-E1D2 sample, the diamond characteristic peak became very strong. The graphite peak is not visible. This condition proves that the layer after implantation is free from graphitic bonds as reported earlier in [8]. The wave number of the first and second order of Silicon peaks was found to be 500 and 1000 cm^{-1} , this is in agreement with the result in [9]. Asymmetry peak profile at wave number 1120 cm^{-1} may be related to the Fano lineshape due to quantum mechanical interference induced by boron dopant. As indicated by the peak at wave number lower than 500 cm^{-1} the intensity of paired boron atoms increased and have tendency of build up at crystalline boundary by increasing of ion dose [11]. This boron atom pair's accumulation is assumed to contribute to the decreasing of carrier mobility and material conductivity.

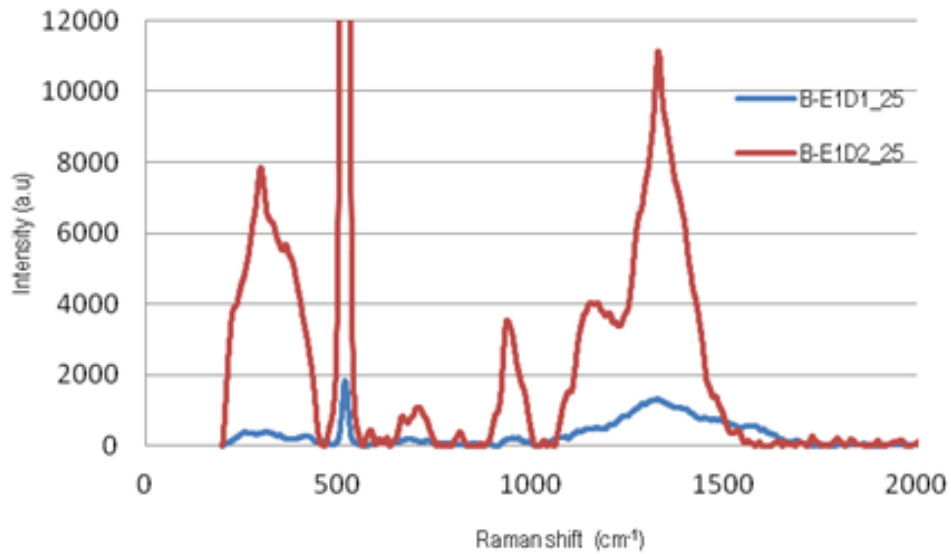


Figure 4. Raman Spectroscopy of B series sample at laser energy E=25mW

Magnetic Properties

The Figure 5 shows the characteristic magnetization curve of the sample B-E1D1 after implantation at 20 keV and dose 1×10^{15} ion cm^{-2} . This curve was measured by VSM with magnetic field up to 1 Tesla (10 kOe) at room temperature. The curve shows a weak ferromagnetic in both parallel and perpendicular to the applied external field direction. The saturated magnetization value M_s is 0.01 emu/gram at applied magnetic field 1 Tesla. This is higher than those presented by Hohne et al. for B3 (c) sample which was irradiated by Boron ion at dose 2.31×10^{16} ions cm^{-2} with $M_s = 0.6 \times 10^{-6}$ emu/6.5mg [5]. It is confirmed, on the B-E1D1 sample the Fe and B ions were incorporated in the film and is believed to improve a ferromagnetic character into the CVD diamond sample, without any indication for an interaction between carbon and iron.

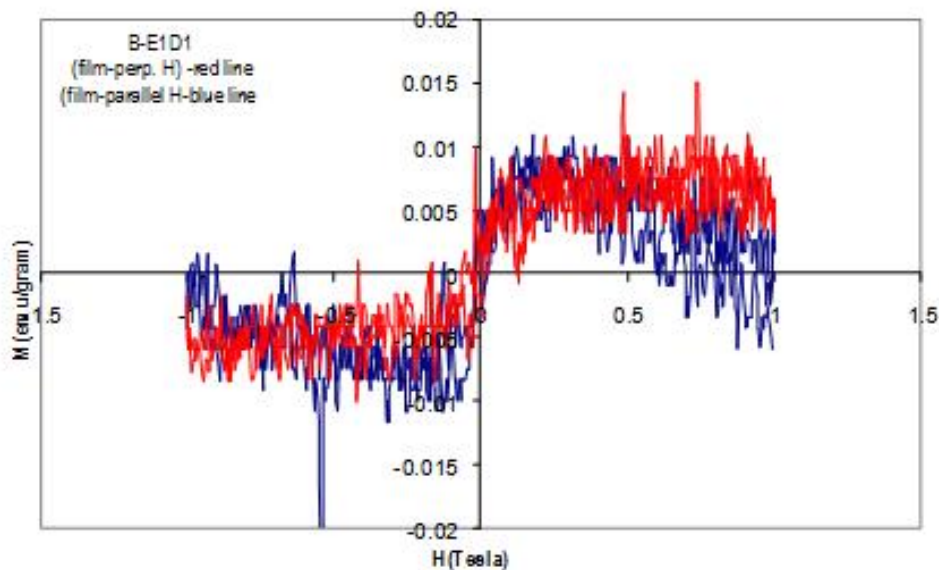


Figure 5. A typical of magnetization curve of CVD diamond film B-E1D1 sample.

Magnetoresistance Properties

The measurement of Magnetoresistance properties were performed by Four Point Probe (FPP) method at room temperature with the external magnetic field up to 8kOe. The effect of Fe+B implantation on the magnetoresistance is shown in Figure 6. The Magnetoresistance ratio of the samples was clearly depend on applied the ion dose. It changes from +45% to +8% at ion doses 1×10^{15} ion cm^{-2} and 1×10^{16} ion cm^{-2} . It is suggested that higher dose caused more damage on the CVD diamond film. In both samples resistance change rate was proportional to $\mu^2 B^2$ at low field and coincidence with other result as reported in [5]. It indicates also that the defects produced by higher doses ion implantation give contributions to the conductivity in diamond film as reported in [10]. Such kind of phenomenon could explain by a localization of the wave function on B-atoms as reported by Willems et al. [12].

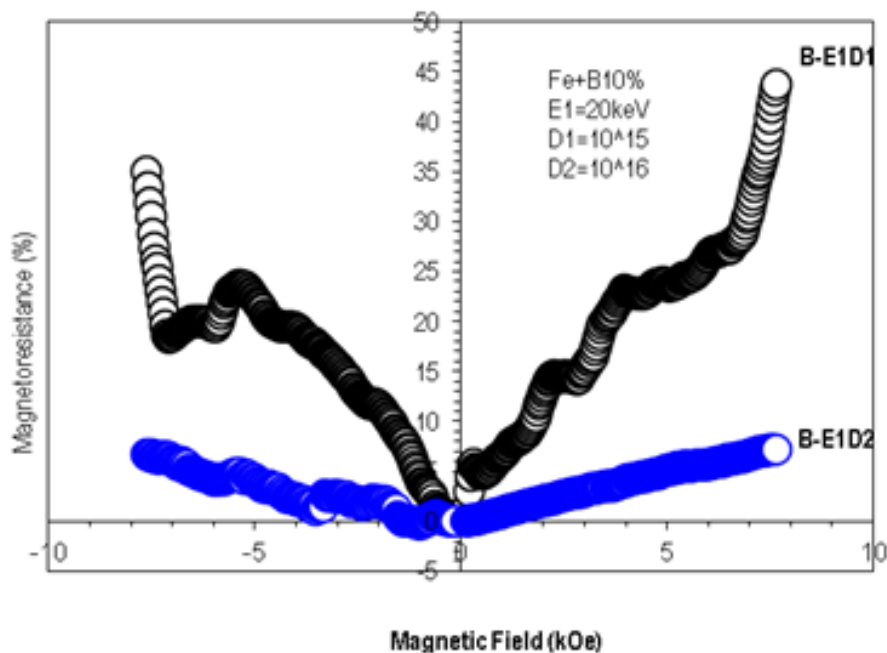


Figure 6. Magnetoresistance curve of CVD diamond film post implanted ion Fe+B

CONCLUSION

In summary, surface modifications of CVD manufactured Diamond Films on Si(111) substrate have been successfully performed by Fe+B ions implantation followed by Argon gas pouring as ion impact growth at accelerated energy 20 and 70 keV and dose 1×10^{15} and 1×10^{16} ion cm^{-2} . TEM equipped with the EELS revealed growth of amorphous carbon layer on top of the Diamond film with thickness of about 100 nm on the implanted sample. Boron atoms have been found incorporated inside the carbon amorphous layer with the relatively homogeneous distribution. This result is in close agreement to the Raman Spectroscopy result which obviously indicates changes on the Raman spectrum due to implantation. The ferromagnetic character of the sample after Fe+B implantation has also been studied. At applied magnetic field of 0.8 Tesla and ion energy 20 keV, the magnetoresistance ratio decreased from +45% on low dose to +8% on high dose.

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