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2009

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J. A. Colón Santana

*University of Nebraska-Lincoln*

Ralph Skomski

*University of Nebraska-Lincoln, rskomski2@unl.edu*

V. R. Singh

*Louisiana State University, Baton Rouge, vrsinghdr@gmail.com*

V. Palshin

*Louisiana State University, Baton Rouge*

A. Petukhov

*South Dakota School of Mines*

*See next page for additional authors*

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Colón Santana, J. A.; Skomski, Ralph; Singh, V. R.; Palshin, V.; Petukhov, A.; Losovyj, Yaroslav B.; Sokolov, Andrei; Dowben, Peter A.; and Ketsman, Ihor, "Magnetism of Cr-Doped Diamond-Like Carbon" (2009). *Peter Dowben Publications*. 218.

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**Authors**

J. A. Colón Santana, Ralph Skomski, V. R. Singh, V. Palshin, A. Petukhov, Yaroslav B. Losovyj, Andrei Sokolov, Peter A. Dowben, and Ihor Ketsman

## Magnetism of Cr-doped diamond-like carbon

J. A. Colón Santana,<sup>1</sup> R. Skomski,<sup>1,a)</sup> V. Singh,<sup>2</sup> V. Palshin,<sup>2</sup> A. Petukhov,<sup>3</sup> Ya. B. Losovyj,<sup>2</sup> A. Sokolov,<sup>1</sup> P. A. Dowben,<sup>1</sup> and I. Ketsman<sup>1</sup>

<sup>1</sup>*Department of Physics and Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, P.O. Box 880111, Lincoln, Nebraska 68588-0111, USA*

<sup>2</sup>*Center for Advanced Microstructures and Devices, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, Louisiana 70806, USA*

<sup>3</sup>*Department of Physics, South Dakota School of Mines, Rapid City, South Dakota 57701, USA*

(Presented 13 November 2008; received 27 August 2008; accepted 26 November 2008; published online 11 March 2009)

Chromium-doped hydrogenated diamond-like carbon (Cr-DLC) and chromium carbide hydrogenated DLC alloys were synthesized by plasma-assisted vapor deposition and investigated by x-ray absorption near edge structure spectroscopy, extended x-ray absorption fine structure, and superconducting quantum interference device (SQUID) magnetometry. Structural and magnetic properties of the doped and alloy materials were investigated as a function of the Cr concentration (0.1–20 at. %). Toward the upper end of the concentration range, Cr precipitates in the form of chromium carbide (Cr<sub>3</sub>C<sub>2</sub>) nanoclusters. For low Cr concentrations, the systems are ferromagnetic at very low temperatures, whereas the chromium carbide clusters appear to be antiferromagnetic with uncompensated spins at the surface. Cr-DLC films and alloys with various Cr concentrations are used to make heterojunctions on silicon, and the produced diodes are investigated by *I-V* measurements. The heterojunctions exhibit negative magnetoresistance that saturates at less than 500 Oe and may be suitable for spin-electronics applications. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072828]

### I. INTRODUCTION

Dilute magnetic semiconductors for spin-electronics application have attracted considerable interest.<sup>1–4</sup> This includes dilute oxides,<sup>5,6</sup> where the dopants form a solid solution in the host lattice, weakly clustered impurities as in Co-doped semiconducting boron carbides,<sup>7–9</sup> and cluster-forming dopants such as cobalt in some oxide dielectrics.<sup>10–14</sup> Less effort has been devoted to wide band-gap materials such as diamond, where the dielectric response is somewhat enhanced but the effective mass is comparatively large.<sup>15</sup> In these structures, which are of interest in optics and spin electronics, the carbon *2p* electrons play a role similar to oxygen *2p* electrons in oxides<sup>16</sup> and to boron *2p* electrons in Co-doped boron carbide.<sup>7–9</sup>

Our focus is on Cr-doped hydrogenated diamondlike carbon (Cr-DLC) and chromium carbide hydrogenated DLC alloys, which we investigate as a mixed matrix material and in the form of heterojunctions for spin-electronics applications. Previous research on similar system indicates that clustering of chromium impurities is expected for concentrations exceeding about 1.5%,<sup>17</sup> although Fan *et al.*<sup>18</sup> reported uniform Cr distribution in C matrix at lower levels (about 6 at. %) and Cr-rich cluster formation at high doping levels of about 12 at. %.

### II. EXPERIMENTAL METHODS

A hybrid plasma-assisted vapor/chemical vapor deposition (PVD/CVD) process<sup>17–19</sup> has been used to deposit the

Cr-DLC films onto a Si(100) substrate. The process involved magnetron sputtering from a Cr target (99.5% Cr) in an Ar/CH<sub>4</sub> discharge with the substrate biased at –1000 V, and the Cr content in the Cr-DLC films was varied by operating the magnetron under current control and modulating the current between 100 and 350 mA, as described in Ref. 17. To determine the chromium content, we have used wavelength-dispersive spectroscopy (WDS) wavelength-dispersive energy dispersive X-ray spectroscopy (WDX/EDAX), extended x-ray absorption fine structure (EXAFS), and x-ray absorption near edge spectroscopy (XANES).<sup>17</sup> X-ray absorption (EXAFS and XANES) spectroscopies were also used to determine the structure of the Cr-DLC films. The x-ray absorption spectroscopy experiments were conducted at the CAMD synchrotron facility at LSU, and a detailed discussion of the x-ray data acquisition and interpretation will be published elsewhere.<sup>20</sup> Superconducting quantum interference device (SQUID) magnetometry was used to perform the magnetic measurements, which were performed with the magnetic field in the film plane.

To gauge potential applications in spin electronics, we have produced heterojunction devices where Cr-DLC films are deposited on *n*-type silicon and chromium acts as a *p*-type dopant. The heterojunction devices were characterized by taking *I-V* and magnetoresistance curves as a function of temperature and Cr concentration.

### III. STRUCTURE

XANES spectra were obtained for the films with Cr contents of about 0.1, 0.4, 1.5, 2.8, and 11.8 at. % along with pure Cr, Cr-III oxide (Cr<sub>2</sub>O<sub>3</sub>), and Cr carbide (Cr<sub>3</sub>C<sub>2</sub>)

<sup>a)</sup>Electronic mail: rskomski@neb.r.com.

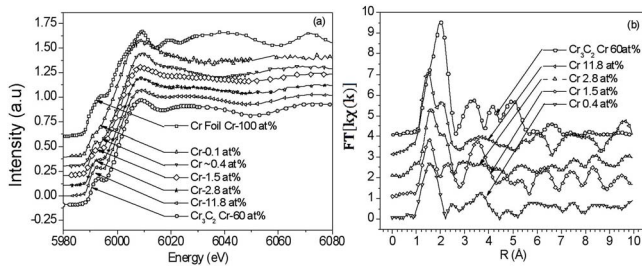


FIG. 1. (Color online) X-ray absorption near edge structure spectra of Cr-DLC films, Cr, and Cr<sub>3</sub>C<sub>2</sub>: (a) normalized spectra translated along the y axis (intensity) and (b) the Fourier transform of the EXAFS spectra for the Cr-DLC films along with pure Cr carbide (Cr<sub>3</sub>C<sub>2</sub>) (Ref. 17).

samples. The XANES spectra indicate that the chemical state and the local environment around the absorbing Cr atoms remain essentially the same<sup>17</sup> for Cr content greater than or equal to 1.5 at. % (Fig. 1). In this concentration range, the XANES spectra of the films are reminiscent of the Cr<sub>3</sub>C<sub>2</sub> spectrum, indicating that high Cr concentrations yield nanocluster precipitates, similar to the situation encountered in Co-DLC (Ref. 21) and Ti-DLC (Ref. 22) systems. For low Cr concentrations (0.4% and 0.1%), the local environment of Cr is characterized by significantly enhanced and reduced C and Cr coordination numbers, respectively. For instance, in the sample with 0.4% Cr, each chromium atom has  $6.6 \pm 0.7$  C and  $2.0 \pm 0.9$  Cr neighbors, as compared to the respective numbers 4 and 11 for Cr<sub>3</sub>C<sub>2</sub> (as determined from fittings to the EXAFS data). This is consistent with a solid solution of Cr in C, with little clustering of Cr. Note that some clustering can never be excluded because the strain created by the substitution of Cr for C yields an attractive interaction (Kanzaki forces) between the Cr atoms, similar to the situation encountered for gases in metals.<sup>23,24</sup>

Figure 1(b) shows the Fourier-transformed EXAFS spectra of Cr carbide and Cr-DLC films at the Cr K edge, as described elsewhere.<sup>17</sup> The spectra of the films with high Cr content (11.8% and 2.8%) show two peaks (1.5 and 2.1 Å) corresponding to the two subshells (Cr,...,C and Cr,...,Cr) of the first coordination shell.<sup>17</sup> The data also suggest a highly disordered (amorphous) structure with some short-range order because no significant features were observed above 2.6 Å. Similar observations were made on these films by x-ray diffraction and low angle x-ray diffraction experiments.<sup>25</sup> Further, as already reported, the bond lengths are nearly the same for all films and similar to that of Cr<sub>3</sub>C<sub>2</sub> powder (2.2 Å for Cr-C and 2.7 Å for Cr-Cr). Valence-band and core-level photoemission indicate that the precipitation of carbide nanoclusters preferentially occurs at the surface.

#### IV. MAGNETIC AND TRANSPORT PROPERTIES

The largely carbon-weighted photoemission features at 6 eV are enhanced at photon energies of about 39–44 eV, near the Cr 3*p* band (42 eV), indicating that the chromium 3*d* bands are strongly hybridized to the carbon 2*p*. This hybridization is the likely reason for the low-temperature ferromagnetism of the dilute Cr-DLC. Below 12 K, the system exhibits ordinary hysteresis loops, with a coercivity of order 0.8 mT (8 Oe), but at somewhat elevated temperatures (above 20

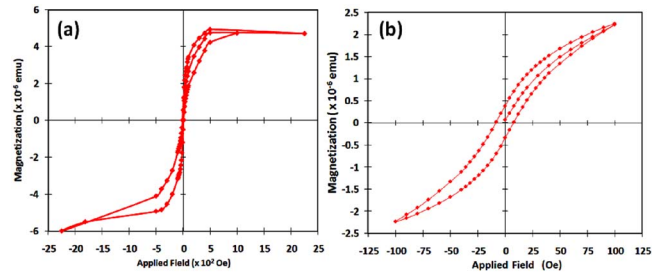


FIG. 2. (Color online) Hysteresis loops and virgin magnetization curves of Cr-DLC with 3% Cr at (a) 20 K and (b) 10 K.

K), the hysteresis loops are constricted (wasplike). Figure 2 shows the magnetization curves of Cr-DLC films with about 3% chromium. Constricted loops frequently occur in inhomogeneous ferromagnets<sup>26</sup> and probably reflect a cluster-size distribution ranging from very few interatomic distances to about 10 nm.

Exchange interactions leading to Curie temperatures above 20 K are common in magnetic oxides and not surprising in the present system, where the C 2*p* electrons strongly hybridize with the Cr 3*d* electrons. In fact, the strong overlap between 2*p* electron orbitals in elements such as B, C, and O means that 2*p* moments created by transition-metal ions and other impurities couple relatively rigidly to neighboring 2*p* atoms. Relatively extended orbitals of this type occur in some oxides<sup>16</sup> and Co-doped semiconducting boron carbides.<sup>7–9</sup>

To gauge the usefulness of the present material for spin-electronics applications, we have fabricated Cr-DLC *heterojunctions* with silicon. We consider chromium a *p*-type dopant of diamond-like materials, which is supported by our ability to make good heterojunction diodes with *n*-type silicon. Figure 3 shows the *I*-*V* curves for heterojunctions made with 11 at. % Cr and 15 at. % Cr contents. At the low doping levels, heterojunction diodes can be made, but the capacitance is quite large and dominates the device properties, consistent with amorphous carbon films on *n*-type silicon.<sup>27,28</sup> The best diode rectification is obtained for 11%–15% Cr doping (Fig. 3). With a Cr doping concentration of

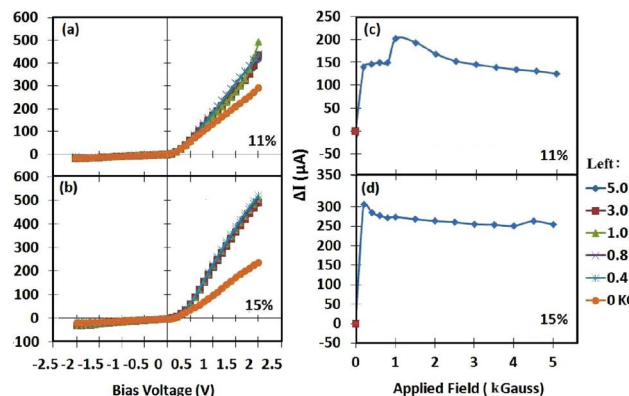


FIG. 3. (Color online) The *I*-*V* curves from the 11 at. % Cr (a) and 15 at. % Cr (b) Cr-DLC film to *n*-type silicon heterojunction devices with changing applied magnetic field at room temperature. The change in forward current, as a function of the magnetic field, for Cr-DLC film to *n*-type silicon heterojunction devices at 11.0 at. % Cr (c) and 15.0 at. % Cr (d) has been plotted for a forward bias of 2 V.

20% or more, the heterojunction diodes with *n*-type silicon show very large relative leakage currents in reverse bias and increasingly resemble a “bad” conventional resistor.

The heterojunction diodes of *n*-type silicon and 11% and 15% Cr-doped DLC films as the *p*-type semiconductor show a strong negative magnetoresistance with the forward bias current increasing with magnetic field, even at room temperature. At 2 V forward bias, the negative magnetoresistance is as much as 50%–100% in an applied magnetic field as small as 300 Oe, as indicated in Fig. 3. The negative magnetoresistance saturates and shows little change at the higher applied magnetic fields, indicating that some magnetic ordering is the origin of this effect. What is the reason for the room-temperature magnetoresistance of these heterojunction diodes? There are no evidence for ferromagnetic ordering in the nanoclusters, but antiferromagnetic order is well known to create uncompensated spins at the clusters' surfaces. These cluster macrospins are likely to interact with each other, especially since the clusters are particularly concentrated at the DLC film surface, with the magnetic field and with an electric current. The coupling mechanisms for high concentrations would then be very different from the low-concentration mechanism.

## V. CONCLUSIONS

In summary, we have investigated Cr-DLC and chromium carbide hydrogenated DLC alloys. In the films of higher chromium concentration, a large coefficient of negative magnetoresistance is observed in heterojunction devices with *n*-type silicon. The negative magnetoresistance of the *I*-*V* curve, which is ascribed to uncompensated spins at the surface of the antiferromagnetic chromium carbide clusters, indicates that the material is suitable for spin-electronics applications.

## ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research (Grant No. N00014-06-1-0616), the Army Research Office (Grant No. DAAG55-98-1-0279), Nebraska MRSEC and NSF (Contract No. ECS 0725881), and NCMN. CAMD is supported by the Louisiana Board of Regents. The authors thank Professor E. I. Meletis and Mr. P. Gupta for their as-

sistance in the deposition experiments and other technical support.

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