Лазерный синтез тонких пленок железа, покрытых углеродом

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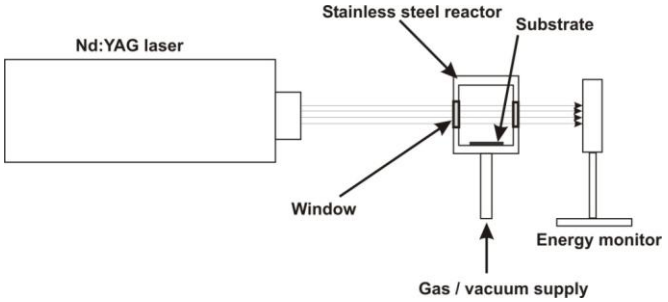
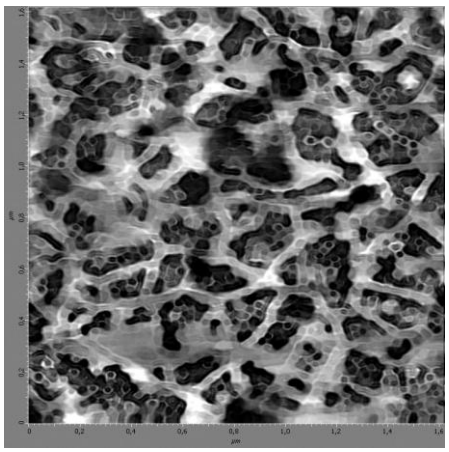
Аннотация

Работа посвящена развитию способа ультрафиолетового лазерного фотосинтеза для производства тонких пленок при комнатных температурах. Продемонстрированы результаты синтеза тонких пленок при помощи фото-диссоциации углеродо- и металлосодержащих соединений. Тонкие пленки железа, покрытые углеродом на подложках из монокристаллического кремния, синтезированы при фотолизе смеси CCl_4 и $Fe(CO)_5$ с аргоном. Фото-диссоциация этой смеси приводит к появлению атомов железа, образующих железное нанопокрытие на подложке и генерации радикалов CCl_3. Предположительно углеродное покрытие растет на железной пленке при взаимодействии молекул CO и радикалов CCl_3 с каталитической поверхностью и образует сетчатую структуру плоских углеродных округлых наноструктур 20÷40 нм в диаметре.

Ключевые слова: тонкие пленки, композитные материалы химическая конденсация паров, покрытия, атомно-силовая микроскопия





Микрофотография нанопокрытия из железных наночастиц, покрытых структурированной углеродной пленкой, синтезированного при фотодиссоциации 30 мбар CCl_4 + 10 мбар $Fe(CO)_5$ в атмосфере аргона. Размер поля 1,6 на 1,6 мкм.

УДК 544.023.223

Laser Based Synthesis of Thin Iron Film Covered by Carbon

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Abstract

This work is devoted to a technique of ultraviolet pulse laser synthesis of thin films at room temperature. The results of thin film synthesis by the photo-dissociation of carbon and metal-bearing compounds are demonstrated. The iron thin film covered by carbon was produced by photolysis of the mixture of CCl_4 and $Fe(CO)_5$ with argon on silicon monocrystalline substrates. Photo-dissociation of this mixture leads to the appearance of iron atoms forming the initial iron coating on the substrate and formation of CCl_3 radicals. Presumably a carbon thin film grows by the interaction of CO and CCl_3 radicals with the iron catalytic surface forming a net structure of flat carbon nanorings with $20 \div 40$ nm in size.

Keywords: thin films, composite materials, chemical vapor deposition (CVD), coatings, atomic force microscopy (AFM).

1. Introduction

The thin iron films on different substrates could be used for microelectronic devices, as a catalytic material for chemical and biology processes. The thin films on the substrates are usually obtained by evaporation and condensation methods. One of the methods is a laser ablation, which provides by the high-energy laser irradiation of the solid targets, resulting in the evaporation of atoms from the surface and their subsequent condensation on the substrate [1]. Another group of methods is the chemical vapor deposition (CVD), where the vapor is formed by the decomposition of gaseous precursors. For example, the precursors can be influenced by being heated to the temperature of thermal decay using the flame, powerful IR laser, microwave discharge and electron beam [2–5]. Another technique for the efficient energy impact on the gas precursor is the ultraviolet (UV) photo-dissociation. The method of UV synthesis of nanoparticles and thin films is characterized by the high process controllability, and the low energy input due to the selective contribution of energy to the breakdown of individual bonds of the precursor molecules. Various metal carbonyls $Me(CO)x$ (namely, $Fe(CO)_5$, $Ni(CO)_4$, $Mo(CO)_6$, $Cr(CO)_6$, etc.) can be used as the precursors for the metal nanoparticles and thin films. The metal carbonyls can be easily decomposed under UV irradiation with wavelengths shorter than 350 nm [6]. The excimer lasers operating on the mixtures Ar–F (193 nm), Kr–F (248 nm), Xe–Cl (308 nm) and Nd:YAG (fourth harmonic 266 nm) can be used for nanomaterial synthesis. The possibility of synthesis of metal nanoparticles using this method was demonstrated in previous works [7-10]. The process of metal thin films synthesis using UV dissociation of metal carbonyls was reported in [11-13]. However, the pure metal nanoparticles and thin films oxidize very fast when they are exposed in air [14]. Thus, for the applications where the purity of the metal is important, the nanostructures should be covered by a protective layer. One of the materials for protection of the metal nanostructures against oxidation could be carbon, which is stable in various aggressive environments. Carbonaceous gaseous compounds or liquids such as C_3O_2, CCl_4, C_2Cl_4, C_6H_6, CH_5OH, CH_4, C_2H_2, and C_2H_4 can be used as the precursors for synthesizing of carbon nanomaterials. According to [15], these compounds

can be subjected to complete photo-dissociation only when the quanta energies correspond to vacuum ultraviolet radiation, i.e., the wavelengths are shorter than 180 nm. However, at a longer wavelength it is possible to decompose noted above carbon precursors up to very active radicals which give the possibility to synthesize carbon structure on the catalytic surface [16]. The carbon nanoparticles synthesis using UV decomposition of C_3O_2 was demonstrated in our previous study [17]. In work by Heszler and co-workers [18] the amorphous carbon films were obtained on Si and SiO_2 substrates upon Ar-F excimer laser induced fragmentation of gas phase C_{60}. The ability to provide ferromagnetic transition metal species encapsulated by graphite has been reported by Dravid and coworkers in [19]. In this paper, we have focused on a deposition technique used to coat iron thin film on the substrate with graphite by the simultaneous UV photo-dissociation of carbon and metal bearing compounds.

2. Experimental setup

In Fig.1 the experimental setup is shown. The stainless steel cell with 1 cm^3 in a volume was used as the photochemical reactor. The substrates are placed in the bottom of the sell. The gas supply line was used for the pumping the cell and filling it with the mixtures of vapors of CCl_4 and $Fe(CO)_5$ with argon prepared in separate vessel. The pressure of the mixture in the reaction cell was kept at 1 bar. The unfocused Nd:Yag laser beam 6 mm in a diameter (SOLAR LQ-129 generated radiation at a wavelength of 266 nm with a pulse duration of 10 ns and maximum pulse energy of 120 mJ) was introduced in the reaction cell throughout the sapphire windows. Thus, the laser activation of the gas phase but not substrate was implemented for thin film synthesis. The experiments were performed in a single pulse mode. After $10 \div 30$ minutes which is sufficient for particles to fall down under natural gravity on the substrate, the substrate was taken out from the reactor and analyzed by atomic force microscope "Solver P47".

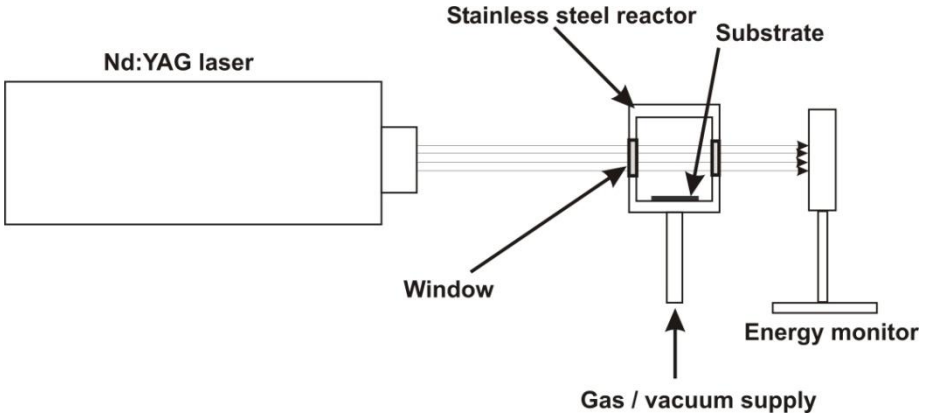

Fig. 1. Experimental setup for thin films synthesis at room temperature

3. Results and discussion

The results of activation of the mixture of 10 mbar $Fe(CO)_5$ diluted in argon and subsequent nanoparticle deposition on the silicon monocrystalline substrate are presented in Fig. 2. In this micrograph several large iron nanoparticle aggregates with $200 \div 400$ nm in size are clearly seen and surrounded by the discontinuous carbon structure consisting of small nanorings with 20 nm in size. The smaller 50 nm aggregates are also presented but worse distinguished. Primary iron nanoparticles formed in gas phase are $10 \div 15$ nm in size [10] and fell down to the substrate under a natural gravity conditions. In this case carbon presumably come from CO molecules formed after photo-dissociation of $Fe(CO)_5$. The carbon structure surrounded the iron aggregates presumably appeared at catalytic decomposition of CO on iron or silicon surface [20]. The next step of synthesis of iron-carbon thin film were carried out using the activation of binary mixture of 30 mbar CCl_4 and 10 mbar $Fe(CO)_5$ diluted in argon. As a result of irradiation the gas phase molecules partly

dissociate with fast formation of iron nanoparticles [9,10] and CCl_3 radicals [16]. As the formed iron nanoparticles have high catalytic activity, hydrocarbon radicals deposit on their surface and decompose with allocation of carbon atoms [16], forming a carbon layer (see Fig. 3, 4). In Fig. 3 the obtained film is presented with low resolution and demonstrates the iron nanoparticle aggregates covered by continuous carbon film. From a micrograph presented in Fig. 4 it is seen that carbon layer consist of the rings around $20 \div 40$ nm in size jointed together.

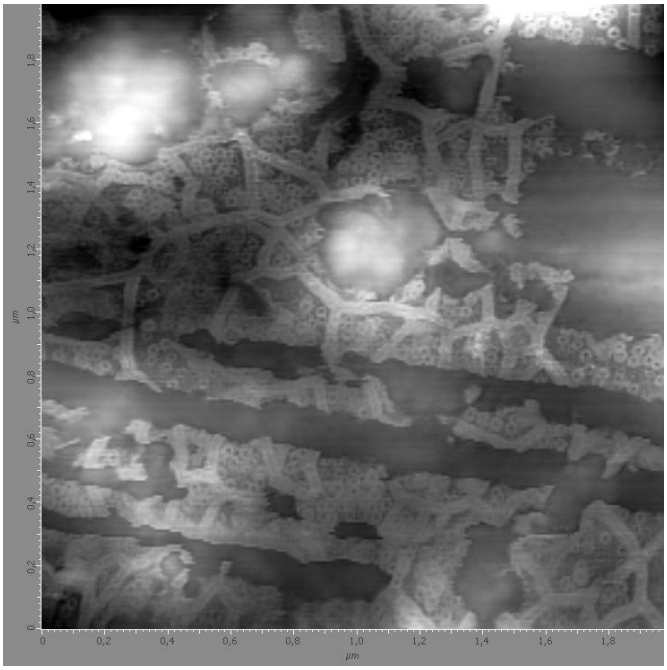

Fig. 2. Micro-photo of iron nanoparticle aggregates formed by photo-dissociation of 10 mbar $Fe(CO)_5$ in argon on silicon monocrystalline substrate. Size of the field is 1.9 on 1.9 microns

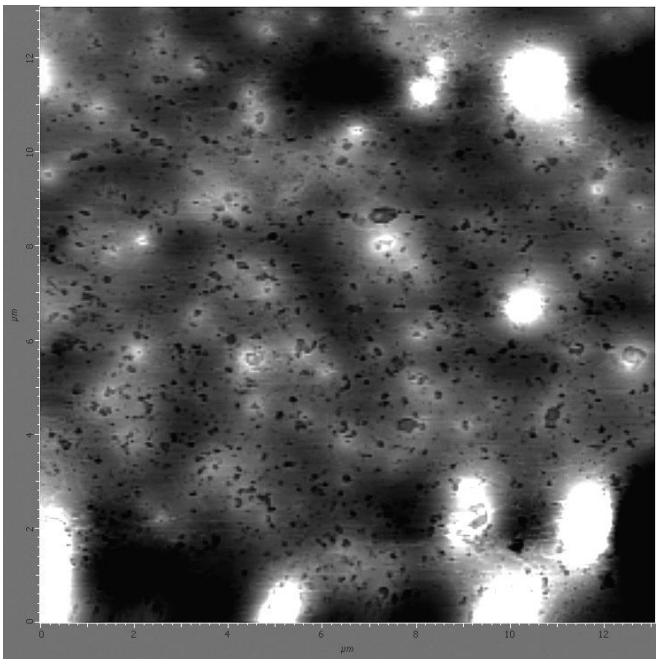

Fig. 3. Microphoto of iron nanoparticle aggregates covered by carbon thin film formed by photo-dissociation of 30 mbar CCl_4 + 10 mbar $Fe(CO)_5$ in argon. Size of the field is 13 on 13 microns

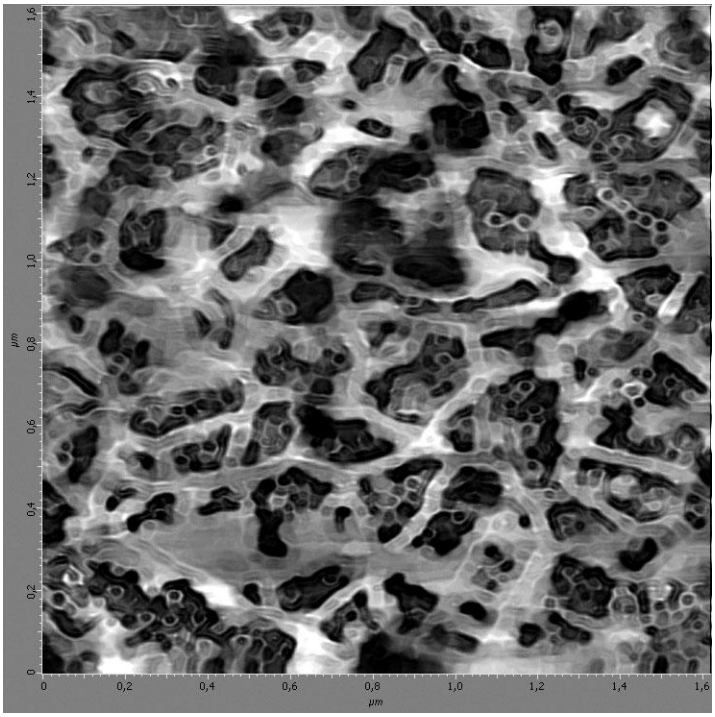

Fig. 4. Micro-photo of iron nanoparticle aggregates covered by structured carbon thin film formed by photo-dissociation of 30 mbar CCl_4 + 10 mbar $Fe(CO)_5$ in argon. Size of the field is 1.6 on 1.6 microns

4. Concluding remarks

In this work the possibility of synthesis of iron-carbon thin films using UV pulse laser photo-dissociation of CCl_4 and $Fe(CO)_5$ was demonstrated. The advantages of this method are the room temperature conditions and low energy input, making it practical for a wide range of applications. The synthesis process is easily controllable, fast, and simple, without the use of high vacuums or high temperature ovens. The carbon structured thin film was synthesized over the iron thin film by activation of the mixture of CCl_4 + $Fe(CO)_5$ in noble gas. The structure of carbon layer consisted of the rings $20 \div 40$ nm in size jointed together. Presumably, the carbon layer could protect the iron thin film against oxidation and degradation in various aggressive environments. The synthesized carbon-iron thin film can be used, for example, for manufacturing of materials for electronics, magnetic sensors, electrodes of fuel cells and protective and absorbing coatings. In addition, the iron thin film on the substrate could be the base plate for carbon nanotube growth by this method as the iron nanoparticles is a good catalyst to form nanotubes from carbon bearing gas species.

Acknowledgment

The authors sincerely acknowledge the financial support by Russian Science Foundation (Grant N 14-50-00124).

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Сообщение поступило в редакцию 11 февраля 2016 г.