Rapid Communication

Chemical Interactions in a Mixture of Gadolinium and Silicon Colloidal Solutions

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A B S T R A C T

We report about the chemical activity of Gd and Si nanoparticles in the mixture of their colloidal solutions. It was found that mixing of two colloids prepared by laser ablation technique results in the chemical interaction between nanoparticles and formation of silicide phases at room temperature. The phase composition of the resulting products was found to be dependent on the mixing order.

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It is known that due to the high surface-to-volume ratio and surface free energy, particles with dimensions at the nanoscale have a strong tendency to coalescence even at much lower temperatures than their melting temperatures as they are put together [1,2]. This feature has been applied for the synthesis of the alloy nanoparticles (NPs) from metals which are immiscible in the solid or molten state [1–4].

The mechanism of the spontaneous alloying is generally interpreted in the framework of defect enhanced diffusion of the elements [5]. Indeed, the lattice of the NPs produced by different synthetic techniques is usually distorted that should favor interdiffusion of the components. The presence of a large number of surface atoms in NPs, defects at the interface or crystal facet changes can enhance the diffusion coefficient. Besides, spontaneous alloying of NPs can be attributed to the melting temperature decrease with the decrease in the particle size [6]. Nevertheless, the detailed kinetics of spontaneous alloying has not been fully elucidated and the interactions in the mixed dispersion of NPs depend on a number of factors, such as the size, surface state of the NPs, the nature of the bimetallic system and solution [4,7].

It should be noted that in the studies on the behavior of NPs in mixtures of colloidal solutions the main attention has been paid to the evolution of their microstructure and alloyed NPs formation, but to the best of our knowledge, there is no published reports on the chemical interaction between NPs and the formation of the compound particles.

In this paper we report about the chemical activity of Gd and Si NPs in the mixture of their colloidal solutions. It was found that a simple mixing of two colloids prepared by laser ablation technique leads to the chemical interaction between NPs and formation of silicide phases

at room temperature. The phase composition of the resulting products was found to depend on the mixing order.

Gd based NPs are of current interest due to their magnetic properties and the potential peculiarities that the nanoscale or nanocomposite materials may exhibit due to their finite size and surface-interface effects. For example, nanoscale Gd, its compounds and alloys can be used as promising materials for applications as therapeutic agents in drug delivery [8,9] and hyperthermia treatment [10,11]. Compared to the materials traditionally used in hyperthermia treatment of tumors, like iron oxide, Gd silicide provides advantage of the heating in the self-controlled regime that makes them the most promising candidates for the hyperthermia application. Knowing the peculiarities of the chemical interactions between Gd and Si nanoparticles in colloidal solutions is important for optimization of the procedure of Gd silicide preparation.

The initial Gd and Si colloids were prepared by laser ablation technique in liquid. Nd:YAG laser (LOTIS TII, LS2134D), operating at 1064 nm (energy 80 mJ/pulse, repetition rate 10 Hz, pulse duration 8 ns) was used for ablation of the relevant target placed in the cell filled with ethanol. After the preparation Gd and Si colloids were mixed in the proportion corresponding to the atomic ratio Gd:Si = 5:4. In order to determine the influence of the mixing order on the process of compound NPs formation, the morphology, composition and structure of the particles prepared by adding Si to Gd and Gd to Si colloids were analyzed by SAED, TEM, HRTEM and FTIR techniques.

The results of the as-prepared NPs morphology studies are shown in Fig. 1. As can be concluded from the TEM images, the prepared Gd and Si NPs are of an overall quasi-spherical morphology and are rather small in size (the average diameter is 5 nm for Si and 10 nm for Gd). However, Gd NPs form aggregates with irregular shape and size more than 100 nm while Si NPs are well-separated and had a narrow size distribution.

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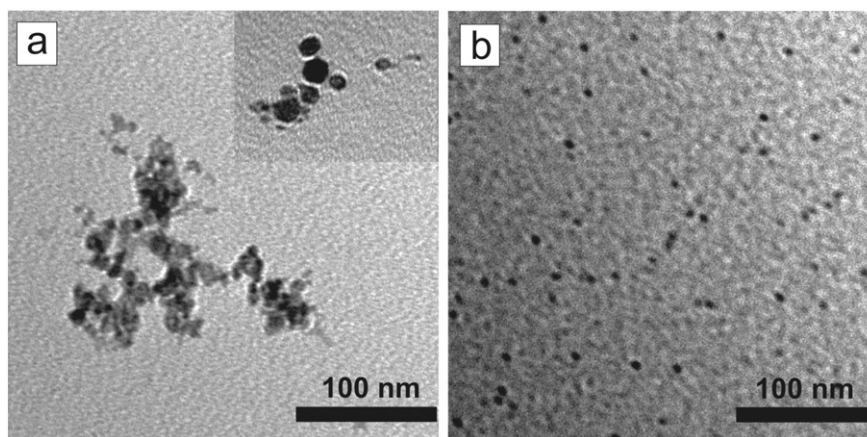E-mail address: n.tarasenko@ifanbel.bas-net.by (N. Tarasenko).

Fig. 1. TEM images of Gd (a) and Si (b) NPs prepared by laser ablation in ethanol.

Addition of silicon colloidal solution to the Gd colloid results in the drastic change in the morphology and structure of the NPs. As can be seen in Fig. 2, several types of NPs appeared: in addition to the small spherical particles, that mostly form aggregates, large near-spherical particles with the diameter more than 70 nm and hollow NPs are formed. The change in morphology (the growth in size) of the particles after mixing can be indicative of their aggregation and coalescence with possible chemical processes between the particles.

The analysis of the SAED patterns of the mixed samples proves that NPs are mostly polycrystalline as well-defined rings are seen in the patterns. However, different types of NPs that are formed after mixing of the colloidal solutions have different composition and crystal structure. Hollow nanoparticles that are shown in Fig. 2 have no Gd phases in their composition while (111), (220) and (311) reflections of cubic silicon are present in the pattern. The formation of the binary Gd_5Si_4 compound is proved by the presence of the reflections from (112), (230), (231) and (114) planes of the orthorhombic Gd_5Si_4 phase (space group *Pnma*, No. 62) [12].

The HRTEM studies of the single particle with diameter more than 100 nm (Fig. 2b) shows that its composition is not uniform throughout the entire volume and the particle can be considered as an aggregate of smaller particles. The analysis of the HRTEM image using the Fourier transformations revealed that the shell of cubic silicon NPs is formed on the periphery of the aggregate. The interplanar distances are measured to be about 0.31 nm, corresponding to the (111) crystal planes of the cubic Si, while the interplanar distances in another direction are

measured to be about 0.19 nm, corresponding to the (220) crystal planes of the cubic Si [13].

In the central part of the particle the area with interplanar distance of 2.8 Å corresponding to the (231) plane of orthorhombic Gd_5Si_4 was found. Observation of several rings in the diffraction patterns allowed determining the lattice parameters of the prepared NPs. The calculated values were found to be $a = 7.42$ Å, $b = 14.84$ Å, $c = 7.82$ Å that is in a good agreement with the reported ones ($a = 7.4857$ Å, $b = 14.750$ Å, $c = 7.7514$ Å) for orthorhombic Gd_5Si_4 [14].

It should be noted that trace amount of carbon (Fig. 2a) or gadolinium carbide (Fig. 2b) phases can also be formed in result of the partial decomposition of ethanol during laser ablation and its reaction with gadolinium.

The order of mixing of the colloidal solutions was found to be the factor that influences the phase composition of NPs in the mixture. As can be concluded from Fig. 3 the morphology of the NPs in mixture does not significantly change with varying of the mixing order. As in the previous case aggregates of small spherical nanoparticles, hollow nanoparticles as well as large near-spherical nanoparticles with non-uniform composition are formed. The analysis of SAED pattern of NPs formed in the mixture of Gd and Si colloids when Gd colloid was added to Si one (Fig. 3a) revealed the formation of the mixture of silicides of Gd_5Si_4 and $GdSi_2$ composition. Besides, some diffraction spots could be assigned to the (111), (220) and (311) planes of cubic Si [13]. It should be noted the orthorhombic GdSi phase has only been found in the large separate spherical NPs formed after mixing of Gd
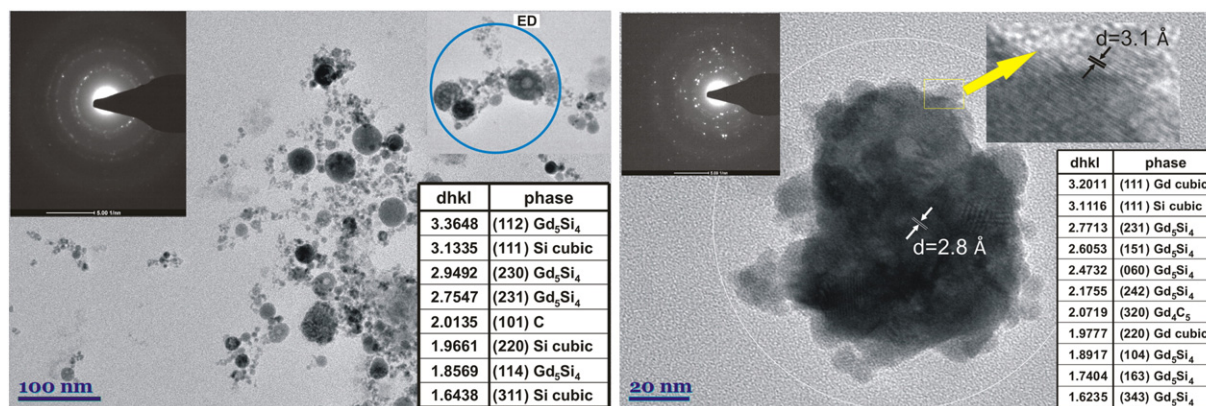

Fig. 2. (a) TEM image of NPs in the mixture of Si and Gd colloidal solutions when Si colloid was added to Gd one. The inset shows the SAED pattern of the selected group of NPs, (b) TEM image and the SAED pattern of the relatively large aggregate formed in the mixture of Si and Gd colloids after adding of Si colloid into Gd colloidal solution.
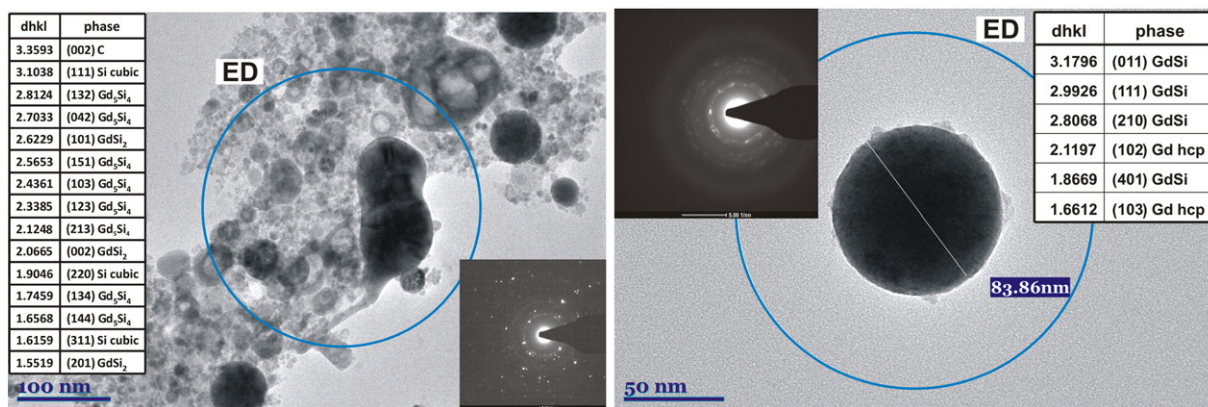
dhkl	phase
3.3593	(002) C
3.1038	(111) Si cubic
2.8124	(132) Gd_5Si_4
2.7033	(042) Gd_5Si_4
2.6229	(101) $GdSi_2$
2.5653	(151) Gd_5Si_4
2.4361	(103) Gd_5Si_4
2.3385	(123) Gd_5Si_4
2.1248	(213) Gd_5Si_4
2.0665	(002) $GdSi_2$
1.9046	(220) Si cubic
1.7459	(134) Gd_5Si_4
1.6568	(144) Gd_5Si_4
1.6159	(311) Si cubic
1.5519	(201) $GdSi_2$

dhkl	phase
3.1796	(011) GdSi
2.9926	(111) GdSi
2.8068	(210) GdSi
2.1197	(102) Gd hcp
1.8669	(401) GdSi
1.6612	(103) Gd hcp

Fig. 3. (a) TEM image of NPs in the mixture of Si and Gd colloidal solutions when Gd colloid was added to Si one. The inset shows the SAED pattern of the selected group of NPs, (b) TEM image and SAED pattern of the relatively large aggregate formed in the mixture of Gd and Si colloids prepared by adding Gd colloid into Si colloidal solution.

and Si colloids (Fig. 3b). In addition, the reflections corresponding to the minor phase of hexagonal Gd were found in the SAED pattern of these particles (Fig. 3b). It is important to note that carbide phases were not found in the fabricated NPs. However, some diffraction spots are related to the graphite phase.

Consequently, the addition of gadolinium to silicon colloidal solution results in the formation of mixture of silicides of different stoichiometry while the addition of silicon to gadolinium colloidal solution is more favorable for the formation of compound Gd_5Si_4 NPs.

Although, to clarify the detailed kinetic of Gd-silicide formation after mixing of the colloids further investigations are required, some suggestions can be done on a base of the performed experiments.

We hypothesize that the formation of compound NPs in the mixed colloidal solution can be explained by spontaneous room temperature interface reaction between Gd and Si NPs in result of their aggregation and coalescence after the particles mixing. Fig. 4 illustrates a possible sequence of processes leading to Gd silicide formation in a mixture of Gd and Si colloidal solutions. Because both types of initial particles are small, they can agglomerate rather rapidly after mixing. The nanoparticles adhere to each other, causing the mutual diffusion of atoms and their chemical interaction.

It should be noted that rare earth metals exhibit rather reactive behavior towards most non-metallic elements of the periodic table, so high interface reactivity [15,16] could therefore be anticipated. Indeed, previously in the works on the deposition of rare-earth metals on the surface of semiconductors [16–18] reactive atomic intermixing was observed that resulted in the compound layer formation on the rare earth metal-semiconductor contacts. In particular the room-temperature chemical reaction on the Gd—Si interface with the formation of gadolinium silicides was observed [15–18] and high interface reactivity was established.

In order to initiate chemical reaction between the interacting NPs, energy of the order of a few electron volts is generally necessary to overcome an activation barrier. The energy releasing in result of the coalescence can serve as a source to overcome an activation barrier and

initiate chemical reaction between the interacting particles [19]. During coalescence, the surface area of the particle decreases, resulting in a heat release associated with the resulting lower surface energy. The heat release associated with particle coalescence may enhance atomic diffusion and reduce the coalescence time.

The amount of energy liberated in result of the coalescence is dependent on the particle size and can be quite large for small particles. For example, estimations showed [19] that a heat release during coalescence of two 3.4 nm Si nanoparticles can result in temperature increase of several hundred degrees.

The energy released upon particle coalescence can be evaluated from the energy balance equation for two coalescing NPs [19], which under adiabatic conditions (without any heat loss to the surroundings) and taking into account the energy released in result of the compound formation can be written as follows:

$$mC_p(T_f - T_0) = \sigma(a_0 - a_f) - \Delta H_f \tag{1}$$

where m is the sum of the masses of the two coalescing particles, C_p is the specific heat of the particle material, T_0 and T_f are the initial and final temperatures of the particle, respectively, a_f – total surface area of the final coalesced nanoparticle, σ is the surface energy per unit area, a_0 – sum of the initial surface areas of two coalescing spherical particles, ΔH_f is the heat of the compound formation.

In Eq. (1), the first term describes the energy change in the coalescing system, the second and the third terms correspond to the heat released due to the reduction in surface energy and in result of the compound formation, respectively.

Eq. (1) was used for estimation of the final temperature of the coalescing NPs. The equation is valid if the coalescence does not result in melting of the nanoparticles. Estimations using Eq. (1) showed that the energy released only in result of the reduction in surface energy of the coalescing spherical 10 nm Gd and 5 nm Si NPs is about 130 eV that provide sufficient energy to overcome an activation barrier and to trigger the chemical reaction [20].
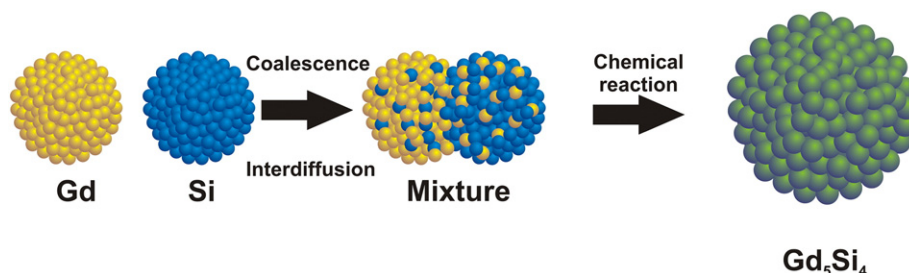

Fig. 4. Illustration a possible sequence of processes leading to Gd silicide formation in a mixture of Gd and Si colloidal NPs.
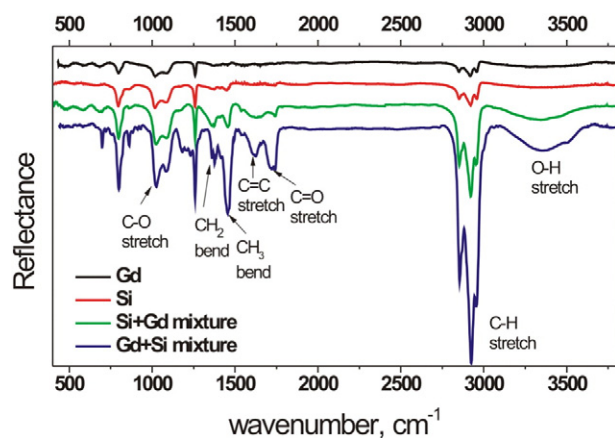
Fig. 5. FTIR spectra of the pristine Gd and Si NPs prepared by laser ablation in ethanol and their mixtures.

Taking into account the heat released in result of the compound formation (ΔH_f) that will further increase the temperature of the particles we could find that coalescence of the spherical Gd and Si NPs with diameters of 10 and 5 nm, respectively, and with initial temperature equal to 298 K with the formation of Gd_5Si_4 could raise the temperature of the final nanoparticle aggregate up to 1230 K. So, the released heat is large enough to promote further reaction of Gd_5Si_4 formation (heat of formation of gadolinium silicide $\Delta H_f = -80$ kJ/mol according to [21]).

The release of heat during coalescence of nanoparticles in our experiment was confirmed by the changes in the FTIR spectra of the particles (Fig. 5). The samples for FTIR investigation were prepared by a deposition of the colloidal particles on the Al plate. The vibrations of O—H, C—H and C—O groups of ethanol have been found in the FTIR spectra of all samples. Mixing of the colloids resulted in the drastic change of the spectra. The emerging of the bands at 1725–1742 and 1617 cm^{-1} indicate the formation of carbonyl group C=O in result of ethanol dehydration and C=C group in result of the ethanol decomposition. These results clearly indicate a thermal decomposition of ethanol due to the energy releasing in result of colloidal NPs mixing. It is noteworthy that the peaks corresponding to Gd—O vibration (540 cm^{-1}) and Si—C (972 cm^{-1}) were not observed in the spectra of all samples.

In summary, our experiments showed that a simple mixing of Gd and Si colloids leads to the chemical interaction between NPs and formation of silicide phases at room temperature. This result can indicate that the lattice of the NPs produced is distorted so interdiffusion of the components is possible. Moreover, the growth in size of the particles after their mixing can be the evidence of their aggregation and coalescence that can result in the compound NPs formation through the interface reactions on the grain boundaries of the aggregated NPs even at room temperature. The phase composition of the resulting products was found to be dependent on the mixing order. The colloidal solution prepared by addition of silicon to gadolinium will be further subjected to laser irradiation with the purpose of the controlled change of nanoparticles composition. Currently laser processing of nanostructures [22] has been recognized as a powerful tool for modification of their morphology and composition.

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