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12-11-2017

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Maria L. Carreon
University of Louisville

Daniel F. Jaramillo-Cabanzo
University of Louisville

Indira Chaudhuri
University of Louisville

Madhu Menon
University of Kentucky, super250@uky.edu

Mahendra K. Sunkara
University of Louisville

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Maria L. Carreon, Daniel F. Jaramillo-Cabanzo, Indira Chaudhuri, Madhu Menon, and Mahendra K. Sunkara

Synergistic interactions of H$_2$ and N$_2$ with molten gallium in the presence of plasma

Maria L. Carreon[a),b)]
Department of Chemical Engineering, University of Louisville, Louisville, Kentucky 40292 and Conn Center for Renewable Energy Research, University of Louisville, Louisville, Kentucky 40292

Daniel F. Jaramillo-Cabanzo[a)]
Department of Chemical Engineering, University of Louisville, Louisville, Kentucky 40292 and Conn Center for Renewable Energy Research, University of Louisville, Louisville, Kentucky 40292

Indira Chaudhuri
Conn Center for Renewable Energy Research, University of Louisville, Louisville, Kentucky 40292

Madhu Menon
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40508

Mahendra K. Sunkara[c)]
Department of Chemical Engineering, University of Louisville, Louisville, Kentucky 40292 and Conn Center for Renewable Energy Research, University of Louisville, Louisville, Kentucky 40292

The present study examines the interaction of hydrogen and nitrogen plasmas with gallium in an effort to gain insights into the mechanisms behind the synergetic effect of plasma and a catalytic metal. Absorption/desorption experiments were performed, accompanied by theoretical-computational calculations. Experiments were carried out in a plasma-enhanced, Ga-packed, batch reactor and entailed monitoring the change in pressure at different temperatures. The results indicated a rapid adsorption/ dissolution of the gas into the molten metal when gallium was exposed to plasma, even at a low temperature of 100 °C. The experimental observations, when hydrogen was used, indicate that gallium acts as a hydrogen sink in the presence of plasma. Similar results were obtained with Ga in the presence of nitrogen plasma. In addition, density functional theory calculations suggest a strong interaction between atomic hydrogen and molten gallium. This interaction is described as a high formation of Ga-H species on the surface, fast diffusion inside the metal, and a steady state concentration of the gas in the bulk. *Published by the AVS.* https://doi.org/10.1116/1.5004540

I. INTRODUCTION

The metal-catalyst-assisted vapor–liquid–solid mechanism has been widely used to synthesize 1D nanomaterials, such as nanowires, by chemical vapor deposition. In this method, the dissociative dissolution of precursors takes place at temperatures above the respective alloy (catalytic metal–material to grow) eutectic temperature. Unfortunately, these temperatures are typically high (<400 °C), making this method unsuitable for large scale manufacturing. A promising approach for achieving the synthesis of 1D nanostructures at low temperatures is to combine low melting point metals such as Ga, In, Al, Sn, and plasma.[1,2] More recently, our experiments using gallium clusters in the presence of a SiH$_4$/H$_2$ (2%) gentle plasma led to the growth of silicon nanowires.[3] In those cases, it was observed that in the absence of plasma, the low melting point metals do not catalyze the growth of 1D materials, suggesting that the selective dissolution of the precursors into the molten metals, compared to the deposition on the substrate, is enhanced by plasma excitation. In other words, synthesis at low

temperatures via these noncatalytic metals can be achieved due to the following: (1) the low melting point metal's capacity to form a eutectic with the precursors at low temperatures and (2) the plasma's ability to dissociate the precursor gases. The combined effect of these two essential elements, a catalyst and plasma excitation, has been termed *plasma catalysis*. Unfortunately, the beneficial effect of plasma excitation and low-melting metals such as gallium has not been understood. If understood properly, this process could be used for growing 1D materials over large areas at low temperatures on different substrates and also for designing plasma catalysts for various chemical reactions.

To explain the effect of plasma excitation in the selective dissolution of solutes in low melting metals is necessary to understand the role of atomic hydrogen. Metal hydrides have been reported as key intermediates in several homogenous and heterogeneous reactions.[4] Particularly, gold hydrides have been postulated as intermediates in numerous homogenously catalyzed hydrogenations[5,6] and hydrosilylations.[7] Despite the wide use of gold as a catalyst, the importance of its hydrides in the catalytic process has recently attracted significant attention.[8] In fact, the strong interaction of gold with hydrogen has been applied for pulling gold nanowires using a hydrogen clamp. In this case, a hydrogen molecule can be incorporated into a gold nanocontact, making a hydrogen clamp that is strong enough to pull a chain of gold atoms.[9]


[a)]M. L. Carreon and D. F. Jaramillo-Cabanzo contributed equally to this work.
[b)]Present address: Department of Chemical Engineering, University of Tulsa, Tulsa, Oklahoma 74104.
[c)]Author to whom correspondence should be addressed; electronic mail: mahendra@louisville.edu

The formation of Ga-H species has been observed as a result of the interaction of supported gallium catalysts with molecular hydrogen at high temperatures.[10] As a matter of fact, gallium has been proposed as a way to store hydrogen through the formation of Ga-H.[11] A clear understanding of the hydrogen adsorption is considered of great importance for the design of molecular sensors and alkane dehydrogenation-aromatization catalysts.[12] The formation of Ga-H species on the Ga_2O_3 surface at elevated temperatures—experimentally detected by Fourier transform infrared spectroscopy—has been attributed to the H adatom that binds to an unsaturated Ga atom.[13] The production of Ga-H species is favored at high temperatures since the creation of oxygen vacancies in Ga_2O_3 increases with temperature. The formation of surface Ga-H on GaN (0001) has also been a topic of intensive research in order to gain a better understanding of the GaN surface structure. Bellitto and collaborators found that molecular hydrogen does not react with the GaN (001) surface, while atomic hydrogen exposure results in the formation of surface Ga-H.[14] However, it is important to mention that the formation of the surface Ga-H species has been reported at high temperatures. Modeling of dissolved hydrogen in Ga-stabilized δ-Pu at low temperatures (less than 300 °C) showed first that in the regions of high Ga concentration, the diffusivity of hydrogen decreases dramatically and second that the H atoms would never enter into these regions.[15]

Plasma excitation similarly enables dissolution of both oxygen and nitrogen radicals into molten metals. In this case, the direct exposure of the plasma excited gas phase over molten metals can result in respective oxide and nitride and oxynitride nanowires.[16,17] The role of plasma excitation here is to enable rapid dissolution of solutes such as oxygen and nitrogen and keeping the surface of molten metal clean for high surface energy. This concept has been exploited for synthesizing oxide nanowires of Zn, Ga, In, Al, and nitrides of Ga, In, etc. The interaction of nitrogen with gallium has already been studied in the presence of plasma for the synthesis of GaN. It has been shown that the presence of plasma helps to break the triple N_2 bond, generating highly reactive radicals such as N, N^+, and N_2^* that make possible the dissolution of nitrogen into gallium.[18] The synergistic effect of plasma activation can be further understood through nitrogen dissolution into low-melting metals. Molecular nitrogen is usually a nonreactive gas under mild temperature and pressure conditions. Typically, conditions of 20 atm and 2000 K are required for dissolving nitrogen in gallium melts using molecular nitrogen according to the reaction represented by Eq. (1). Using plasma activation of nitrogen, the dissolution into molten gallium, Eq. (2), is favored at subatmospheric pressures and temperatures as low as 850 °C.[18,19] It has been concluded that the recombination rate of N to form N_2 is slow enough to allow the formation of GaN.[20] Such interactions have been exploited to grow GaN nanowires under self-catalyzed conditions using nitrogen as a precursor with the help of plasma at temperatures slightly below its decomposition temperatures of 900–1000 °C,

$$Ga(l) + 1/2N_2(g) = GaN(s), \qquad (1)$$

$$Ga(l) + N(g) = GaN(s). \qquad (2)$$
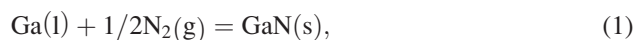
A better understanding of the interaction of molten gallium with hydrogen and nitrogen plasmas at low temperatures can aid in the possibility of applying this synergistic effect to several other areas of great interest, such as plasma catalysis.

II. EXPERIMENT

In the present study, absorption/desorption experiments as well as theoretical-computational calculations were performed in an effort to demonstrate the synergistic effect of plasma and molten gallium. The experiments were carried out in a custom-built, capacitively coupled, radio-frequency (RF) plasma batch reactor, Fig. 1. The reaction is conducted in a 30-mm-diameter quartz tube (90 cm in length) that is placed inside a tube furnace with temperature control. The gases are fed at the front end of the tube, and the two-concave stainless steel parallel plate plasma electrodes are positioned outside the tube between the gases inlet and the tube furnace, immediately adjacent to the furnace. The working electrode is connected to a 600 W, 13.6 MHz, RF power generator (Seren R601) through an automatic matching network controller (Seren MC2). This configuration allows the control of the forward power and the reduction of the reflected power to zero during operation. The counter electrode is connected to a common ground. During operation, the glow discharge region of the plasma extends to approximate 45 cm into the tube furnace. Vacuum is achieved using a roughing pump, and pressure is measured downstream the tube using an absolute capacitance manometer with an accuracy of ±0.50% at the pressures observed during this study. Each experiment was performed as follows: A section of the chamber (10–15 cm) was packed with inert supports either coated or uncoated with gallium. When coated, the typical amount employed was 4 g. Later, the chamber was set to the experiment temperature and then was filled with the chosen gas (hydrogen or nitrogen) until the desire initial pressure was reached. At this point, the pressure as a function of time was started to be recorded. After 12 min—allowing the system to reach equilibrium—the plasma was ignited and the plasma–catalyst interaction was initiated. The supports were exposed to plasma for 30 min. Once the exposure time was achieved, the plasma was shut down. Data were recorded for additionally 30 min.

Experimental results were complimented with a molecular dynamics study in an effort to gain a microscopic understanding of the interaction of hydrogen with molten Ga. The *ab initio*
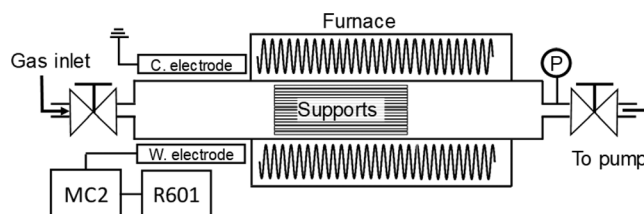

FIG. 1. Schematic of the system used during experimentation.

density functional theory (DFT)[21,22] in the generalized gradient approximation and the Perdew-Burke-Ernzerhof[23] approach as implemented in the Vienna *ab initio* simulation package[24] were used in this study. The projected augmented wave potential[25] is used to describe the core electrons. A kinetic energy cutoff of 550 eV was found to be sufficient to achieve a total energy convergence of the energies of the systems to within 1 meV.

III. RESULTS AND DISCUSSION

Absorption/desorption experiments for hydrogen, Fig. 2, show a dissimilar behavior between the coated and uncoated supports. When no gallium was used and while the plasma is on, there is an increment in the overall pressure, followed by a slow decrement when the plasma is shut off. This observation is explained as follows: as mentioned in Sec. II, the plasma discharge does not extend throughout the whole tube. It is believed that this causes a dynamic system where radicals formed in the plasma region diffuse into the nonplasma region and recombine, while molecules diffuse from the nonplasma region to the electrodes and are dissociated into radicals. The difference between the rate of formation of radicals, due to dissociation of molecules entering the electrodes' region, and the rate of recombination of the radicals that diffuse from the plasma region to the nonplasma region determines the net increment/decrement of species inside the chamber. This effect is believed to give rise to the two distinct regimes observed in Fig. 2. The first regime is distinguished by a rapid initial increase in the pressure followed by stabilization, and it is explained by an overall increment of moles due to the plasma excitation. Conversely, the second regime is marked by a linear increment of pressure over time, obeying standard diffusion processes. When the gallium-coated capillaries were introduced, a dramatic pressure drop is evidenced when the plasma is ignited followed by a slow increment when the plasma is shut off. This result suggests that the rate of adsorption/dissolution of the gas species into the molten metal is faster than the rates of desorption and production of radicals.

FIG. 3. Adsorption/desorption measurements in terms of pressure change when uncoated or Ga-coated supports were exposed to nitrogen plasma. Experiments were performed at 400 °C and a power of 100 W.

The exponential decay shape of the pressure curve—while the plasma is on—indicates that the metal is saturating and the rate of adsorption is diminishing as the experiment is conducted. Interestingly, an analogous behavior was observed for nitrogen (Fig. 3).

To understand the different regimes in the system, new experiments were performed. Coated and uncoated capillaries were exposed intermittently, 10 min at the time, to hydrogen and nitrogen plasmas, Figs. 4 and 5, respectively. Similar

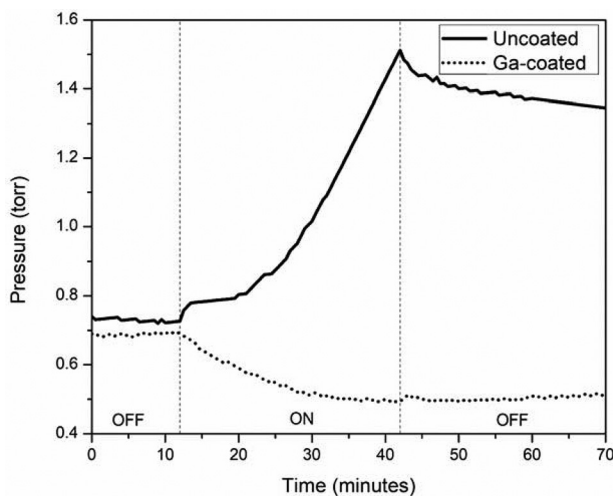FIG. 2. Adsorption/desorption measurements in terms of pressure change when uncoated or Ga-coated supports were exposed to hydrogen plasma. Experiments were performed at 400 °C and a power of 100 W.
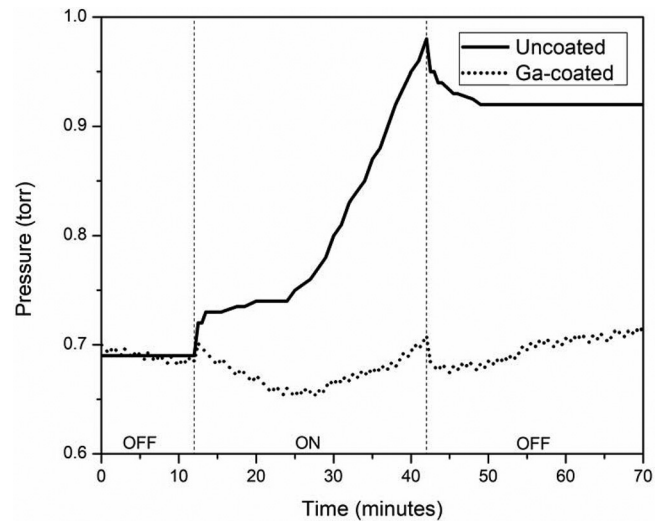

FIG. 4. On/off experiments. Change in pressure when uncoated (top) and Ga-coated (bottom) supports were intermittently exposed to hydrogen plasma. Experiments were performed at 400 °C and a power of 100 W.
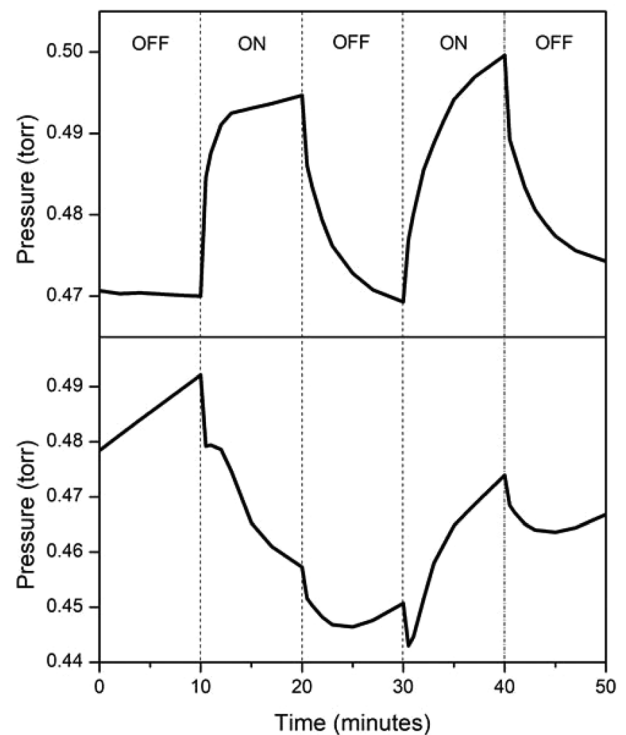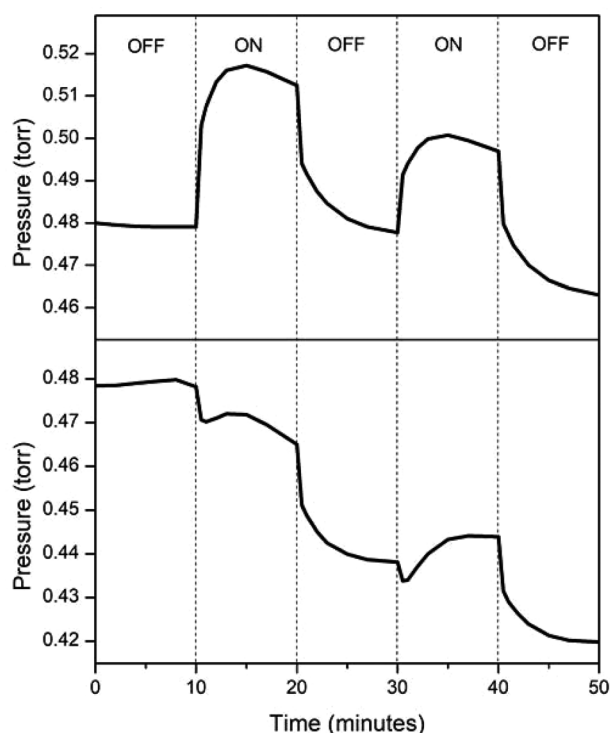
FIG. 5. On/off experiments. Change in pressure when uncoated (top) and Ga-coated (bottom) supports were intermittently exposed to nitrogen plasma. Experiments were performed at 400 °C and a power of 100 W.

results were obtained for both gases. By limiting the plasma exposure to 10 min, it was possible to identify the different phenomena that are taking place in the process. During the first 10 min of plasma exposure, the uncoated and coated capillaries behaved differently but in good agreement with the results previously presented in Figs. 2 and 3. The increment in pressure observed when the uncoated capillaries were exposed to plasma follows the same behavior as the first regime explained hereinbefore, suggesting that, by reducing the plasma exposure time, the diffusion effects are limited. The opposite behavior was observed when coated capillaries were used, i.e., a rapid decrease in pressure followed by stabilization followed by an exponential decay in pressure. In the case of nitrogen, a slight increase before the exponential decay was perceived. Once the plasma was shut off, the pressure decreased for both cases. Nonetheless, when gallium was used, the decrement rate was slower. In the case of hydrogen after approximately 5 min of shutting the plasma off, the pressure started to increase. The difference between both cases indicates that while the decrease in pressure of the system without gallium is a response exclusively of the almost instantaneous recombination of radicals, the system with gallium-coated capillaries presents two different coexisting phenomena. The recombination of radicals due to the lack of plasma excitation and the desorption of species from the molten metal is suspected to be responsible for the overall number of species in that system. The samples were exposed to plasma for 10 minutes one more time. The results show a similar response in pressure in the gallium free configuration compared to the response obtained during the first plasma

exposure, whereas the pressure in the other system decreases initially and then increases. The shape of the curve once the pressure increases is similar to the curve obtained in the system without gallium, suggesting that the metal got saturated, reducing considerably the amount of species that are being dissolved and acting like a noncatalytic material. Finally, the pressure after shutting the plasma off was monitored for extra 10 min. The curves obtained in this period are in accordance with the ones obtained the first time the plasma was turned off.

The moles of hydrogen and nitrogen absorbed into the molten metal per gram of Ga in the presence of plasma (70 and 140 W) at different temperatures were calculated (Fig. 6). As observed from the plot, when the molten gallium is exposed to a 70 W hydrogen plasma, the amount of hydrogen absorbed increases from 100 to 200 °C, when absorption reaches its maximum, and then decreases consistently as the temperature increases. This temperature sets the limit where the rate of desorption of hydrogen becomes significant. When the plasma power is doubled to 140 W, it is observed
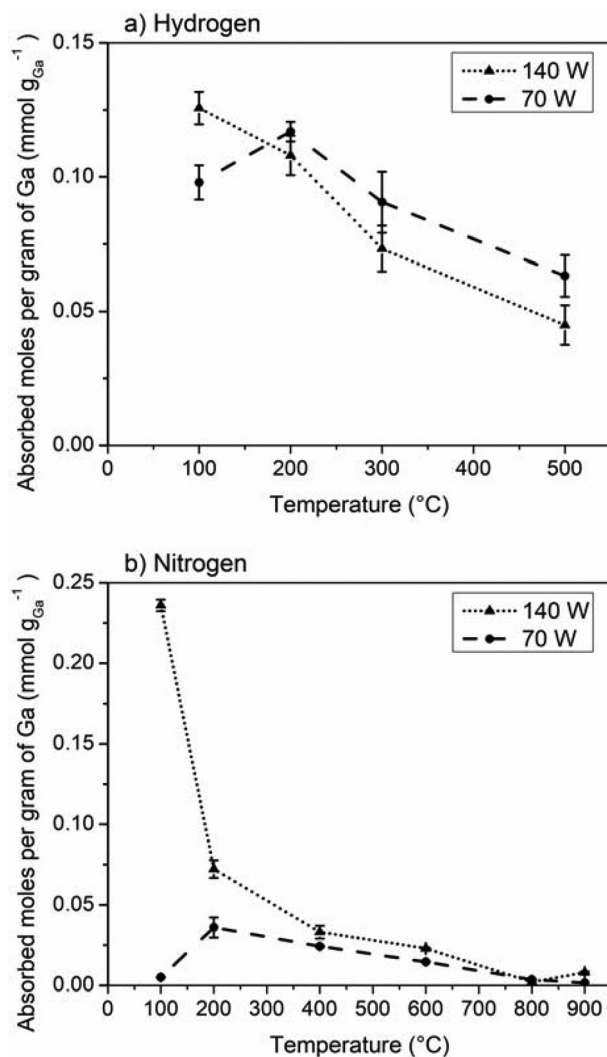

FIG. 6. Absorbed moles per gram of Ga of (a) hydrogen and (b) nitrogen into the molten gallium as a function of temperature under 70 and 140 W RF-plasma exposure.
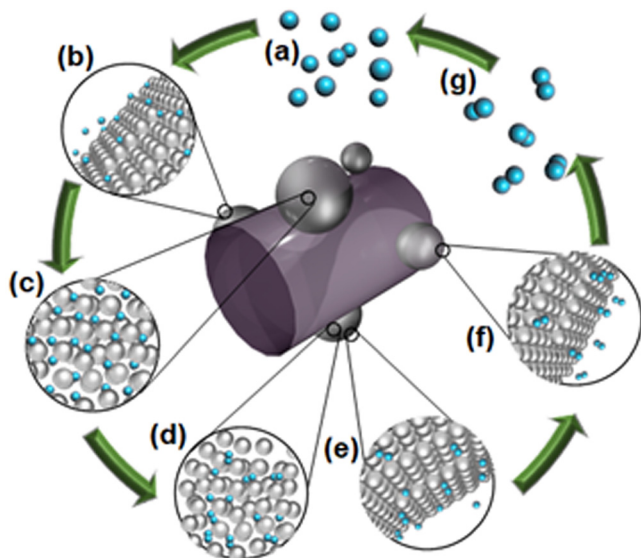
FIG. 7. (Color online) Proposed mechanism: (a) creation of atomic species, (b) surface adsorption, (c) diffusion into the bulk, (d) recombination inside the bulk, (e) surface recombination, (f) desorption of molecular species, and (g) molecular species in the gas phase.

that for temperatures higher than 200 °C, the number of moles absorbed reduces; this behavior can be attributed to a higher local temperature of the Ga droplets, due to the absorption of the heat released during the recombination of radicals,[26] which leads to a higher desorption rate. A similar behavior is seen for nitrogen absorption, where high temperatures lead to high desorption rates and therefore low absorption of nitrogen. The existence of this interaction at low temperatures is of great importance because it can lead to the possibility of synthesizing ammonia at mild conditions.

The overall interaction of molecular hydrogen with molten Ga is proposed to be as follows: (1) creation of atomic hydrogen species; (2) surface adsorption of hydrogen on molten gallium, i.e., formation of Ga-H species; (3) diffusion of H or Ga-H into bulk; (4) recombination inside the gallium bulk; (5) surface recombination between atomic hydrogen in the gas phase and adsorbed species on the surface; and (6) desorption of molecular hydrogen. A graphical representation of the mechanism is presented in Fig. 7. Hydrogen was chosen as an illustrative example; it is believed that the mechanism for the interaction of molecular nitrogen with molten gallium is the same.

Besides the diffusion and the desorption steps, all the steps can be represented by a chemical reaction. The enthalpy of

reaction (ΔH_{rxn}) of a particular reaction can be estimated by subtracting the total energy of the bonds formed from the sum of the broken bonds' energy, Eq. (3). This approximation becomes useful for determining the thermal behavior of a reaction; for example, when the bonds that are being broken are stronger than the ones that are being formed ($\Delta H_{rxn} > 0$), the reaction will be endothermic. This expression does not provide exact values for ΔH_{rxn} because it uses average bond energies. The bond enthalpy of a chemical bond depends upon the molecular environment in which the bond exists. Therefore, the bond energy values reported in the literature are averaged. Table I presents the different reactions that take place in the gallium-hydrogen/nitrogen system with their respective ΔH_{rxn}. In the case of hydrogen, it is important to notice that while the surface adsorption and the surface recombination processes are exothermic, the gas dissociation and the bulk recombination are endothermic. It is believed that the energy in the gas dissociation step is supplied principally by the RF generator, whereas the energy in the bulk recombination step is provided by the temperature of the system. Accordingly, while bulk recombination rates should increase with increasing temperatures, the production of radicals should remain unaffected, independent of temperatures, thus leading to a decrease in the quantity of moles absorbed. Even though the bulk recombination of nitrogen atoms is exothermic, this energy is smaller in magnitude than both the surface adsorption and the surface recombination, which explains why the bulk recombination is favored over the other reactions at higher temperatures. Experimental data, Fig. 6, confirm this behavior: the higher the temperature, the lower the number of molecules absorbed,

$$\Delta H_{rxn} \approx \sum (\text{broken bond energy}) - \sum (\text{formed bond energy}). \quad (3)$$

Hydrogen and nitrogen atoms recombine differently on dissimilar surfaces. Rahman and Linnett studied the recombination of nitrogen on pyrex and different metals. In the case of Pyrex surfaces, they found that the recombination of nitrogen is first order at pressures ~0.1 Torr; a second order process is noticeable at higher pressures (i.e., 0.9 Torr). Because of this observation, the authors proposed that both Hinshelwood and Rideal mechanisms occur on a varying sticking coefficient surface. In their study, the recombination coefficient, γ, which is defined as the fraction of atoms striking the surface which recombine, was reported in the order of

TABLE I. Chemical reactions and their enthalpy of formation for the Ga-H₂ and Ga-N₂ systems.

	Hydrogen			Nitrogen		
	Reaction		ΔH_{rxn} (kJ/mol)	Reaction		ΔH_{rxn} (kJ/mol)
Gas dissociation	$H_2 \rightarrow H + H$	(4)	436 (Ref. 27)	$N_2 \rightarrow N + N$	(5)	945 (Ref. 27)
Surface adsorption	$Ga + H \rightarrow Ga–H$	(6)	−262 (Ref. 28)	$Ga + N \rightarrow Ga–N$	(7)	−218 (Ref. 29)
Surface recombination	$Ga–H + H \rightarrow Ga + H_2$	(8)	−174[a]	$Ga–N + N \rightarrow Ga + N_2$	(9)	−727[a]
Bulk recombination	$Ga–H + Ga − H \rightarrow 2Ga + H_2$	(10)	88[a]	$Ga–N + Ga − N \rightarrow 2Ga + N_2$	(11)	−509[a]

[a]Enthalpies calculated using Eq. (3) and reported bond energies [Eqs. (4)–(7)].

10^{-6}.[30] In another study, Rahman and Linnett presented γ_N for different metals: 2×10^{-3}, 6.7×10^{-5}, and 6.8×10^{-2} for Fe, Ni, and Cu, respectively.[31] Argoitia *et al.* exposed molten gallium to nitrogen plasma at low pressure. They found that the surface recombination is slow enough that nitrogen atoms diffuse into the bulk and form GaN crystals.[18]

In the case of hydrogen radical recombination on surfaces, Wood and Wise reported that the formation of a hydrogen molecule from two hydrogen atoms on Pyrex glass and fused quartz surfaces occurs through two varying mechanisms: Rideal (R) and Hinshelwood (Hi) with two binding states: strongly bound (a) and weakly bound (b). They concluded that the overall recombination of hydrogen is composed of four different regimes: Rideal-strongly bound (R-a), Rideal-weakly bound (R-b), Hinshelwood-strongly bound (Hi-a), and Hinshelwood-weakly bound (Hi-b). Depending on the temperature, one of these terms becomes dominant. Specifically, Hi-a, Hi-a, Hi-b, and R-b are the predominant regimes for temperatures >500, 500–120, 120–50, and <50 K, respectively. Additionally, Wood and Wise reported a recombination coefficient in the order of 10^{-3}, as well as recombination rates of $\sim 10^{17}$ and $\sim 10^{15}$ atoms/cm^{2}s at 500 and 77 K, respectively.[32] The recombination of hydrogen onto diamond has also been reported. Gat and Angus found that for this system, $1 > \gamma > 0.23$ with a recombination rate of $\sim 10^{19}$ atoms/cm^2 s. The authors suggest that due to this high recombination rate and the exothermic behavior of the reaction, much of the energy that reaches the surface during diamond deposition is transported by atomic hydrogen.[26] In the case of metals, recombination of hydrogen atoms is strongly dependent on the metal surface where atoms recombine. Melin and Madix reported the hydrogen recombination coefficient on Ag (0.05), Au (0.03), Co (0.13), Cu (0.09), Fe (0.1), Ni (0.1), Pt (0.06), and W (0.08).[33] Furthermore, hydrogen atoms can migrate freely in the bulk and may segregate between the bulk and the surface.[34] Specifically, for metals in the presence of plasma where reactive species exist (i.e., free radicals, excited molecules, and ions), it has been reported that the surface coverage of selected species like H-atoms can be easily achieved. As the H-coverage increases and a threshold of H-coverage is passed, the surface H-atoms start to diffuse to the subsurface. It has been found that as the H-coverage increases, the activation energy for associative desorption of H$_2$ decreases.[35] Nevertheless, the diffusion of hydrogen into molten gallium, as well as the stability of hydrogen atoms on the surface of molten gallium, has not been studied. In order to gain a better understanding of the diffusive nature of hydrogen in gallium, which is a main step in the mechanism proposed, a computational study is presented.

The simulations were conducted using DFT. The initial starting geometry of the bulk gallium is simulated using a 216 atom orthorhombic supercell. The size of the supercell is large enough to capture the interaction details accurately. The initial configuration was heated at 3000 K (well above the melting temperature), which forces the system to lose the memory of the initial configuration and equilibrates at this temperature. The system is then rapidly quenched to 350 K, then slowly quenched from 350 to 300 K, and finally equilibrated at 300 K. The Brillouin zone of the supercell lattice is sampled with the Gamma point (k = 0). The results were checked for convergence by considering a higher cutoff energy (>550 eV) and additional k-points which affected the detailed atomic motions only slightly with no change in the general picture. The system obtained was found to be amorphous and contains both under-coordinated and over-coordinated gallium atoms.

To investigate the interaction between hydrogen atoms and molten gallium, 60 hydrogen atoms were added at the undercoordinated sites. The model was quenched further to reach 0 K, allowing the structure to relax at 0 K and finding the nearest local minimum energy configuration (amorphous state). The combined amorphous Ga and H system was heated to 300 K and equilibrated by running the simulations for another 2 ps [Fig. 8(a)]. The system was then heated to 600 K, and the whole process was repeated to obtain the structure shown in Fig. 8(b). The calculated mean square displacement (MSD) plots for the combined Ga and H systems at 300 and 600 K (supplementary material)[36] suggest a very diffusive nature of hydrogen atoms in the gallium bulk with a higher diffusivity at 600 K than 300 K. This observation is validated by the linear increase of the MSD with time.

To model the interaction of hydrogen with molten gallium's surface, a slab geometry, extracted from the amorphous structure of Ga at 0 K [see Figs. 9(a) and 9(b)], was considered. A vacuum space of 15 Å was added along the z-direction of the systems perpendicular to the surface plane to prevent any erroneous interference from interactions between images replicated along the z-axis. The system was relaxed again using the DFT methods. Subsequently, hydrogen atoms at the undercoordinated Ga sites of the upper surface of the slab at 0 K were added, and then, the new geometry was optimized to find the minimum energy configuration. The hydrogenated relaxed slab was then annealed and equilibrated at 600 K to study the behavior of hydrogens on the gallium surface. While observing the trajectory of the
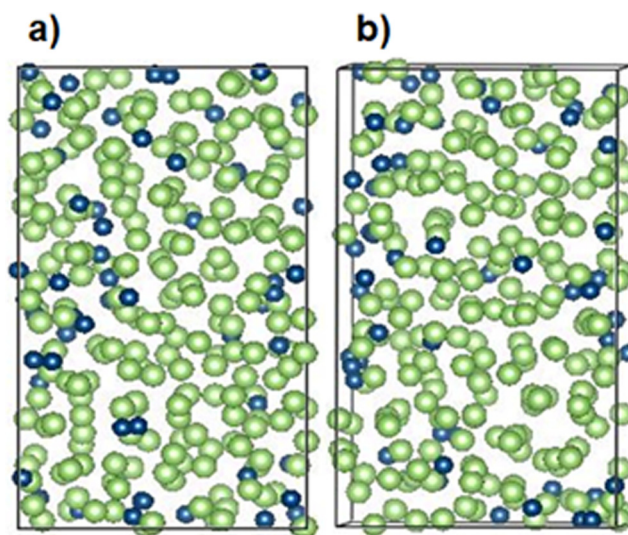

Fig. 8. (Color online) Combined Ga and H system at (a) 300 K and (b) 600 K.
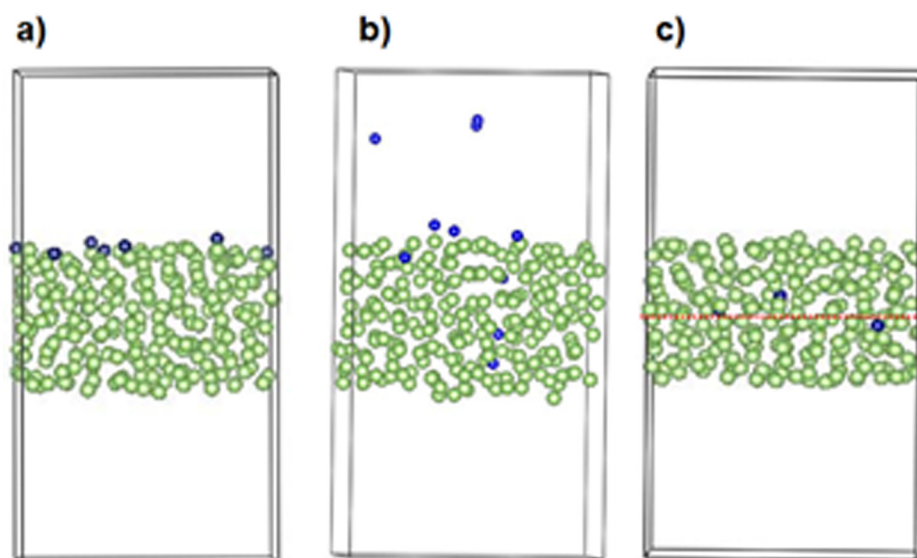
F_IG. 9. (Color online) (a) Slab geometry showing hydrogens added on the Ga surface. (b) After annealing and equilibrating at 600 K, three hydrogens are found to diffuse into the interior of the slab, while the rest are seen to be moving on the surface and above the surface. (c) Three hydrogens are inserted at the intermediate positions inside the slab. After annealing and equilibrating at 600 K, one hydrogen is found to be trapped inside the slab, while the other two are seen to be moving toward the surface.

hydrogen atoms, most of the hydrogen atoms appeared to simply execute a hovering movement on the surface and above the surface (in the empty space of the cell along the z-axis). Three hydrogens were found to diffuse into the slab. The hydrogen atoms remaining on the surface are seen to be very unstable due to the thermal fluctuation of the gallium atoms and the floating bonds of the gallium atoms. The diffusion of the hydrogen atoms inside the slab can be considered as a spontaneous event as the thermal fluctuations at 600 K are found to be high. The bonding between hydrogen and the surface Ga atoms is rather weak with bond lengths between 1.6 and 1.8 Å at 600 K during the diffusion process.

To gain further insight into the diffusion process, a new set of DFT simulations was performed by adding three hydrogens at the interstitial sites in the middle of the amorphous gallium slab. The system obtained is heated to 600 K and equilibrated at this temperature. Two of the hydrogen atoms diffused toward the surface, while the third one remained trapped inside the slab. The diffusive nature of the hydrogens in molten gallium can be attributed to the weak interaction between gallium and hydrogen resulting from the thermal vibrations and the interaction with the over-coordinated gallium atoms in the system at high temperature. Our simulation results indicate a high diffusivity of hydrogen in molten gallium and instability of hydrogen atoms on gallium's surface and are in agreement with the experimental observation that at high temperature, the recombination in the bulk becomes the dominant step of the process, resulting in a lower adsorption of hydrogen as depicted in Fig. 9(c).

IV. SUMMARY AND CONCLUSIONS

The existence of a synergism between gallium and hydrogen/nitrogen plasmas at low temperatures was observed. The overall interaction of molecular hydrogen with molten gallium is composed of multiple simultaneous processes: Surface adsorption, diffusion into the bulk, recombination inside the bulk, surface recombination, and desorption of species from the bulk. Depending on the conditions, some processes become dominant. It was found that the amount of hydrogen/nitrogen adsorbed was inversely proportional to both temperature and plasma power, suggesting that the dissolution of species is promoted at higher temperatures. The interaction between gallium and hydrogen/nitrogen in the presence of plasma is primarily observed at low temperatures and can be employed to address several technological challenges such as the synthesis of gallium nitride and ammonia at mild conditions. The simulations conducted using Density Functional Theory (DFT) presented herein confirm a high diffusing behavior of hydrogen into molten gallium even at low temperatures.

ACKNOWLEDGMENTS

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[36]See supplementary material at http://dx.doi.org/10.1116/1.5004540 for details on the experimental set up and the Ga-H interaction modeling.