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# Effect of surface treatment with different sulfide solutions on the ultrafast dynamics of photogenerated carriers in GaAs(100)

Mikhail V. Lebedev[a,*], Katsuyoshi Ikeda[b,c,d], Hidenori Noguchi[b,c,d,e], Yusuke Abe[b], Kohei Uosaki[b,d,e]

a A. F. Ioffe Physical-Technical Institute, Russian Academy of Sciences, Politekhnicheskaya 26, St. Petersburg 194021, Russia

b Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

c PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

d Global Research Center for Environmental and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan

e International Center for Materials Nanoarchitectonics (WPI-MANA), NIMS, Namiki 1-1, Tsukuba 305-0044, Japan

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∗ Corresponding author. E-mail address: mleb@triat.ioffe.ru (M.V. Lebedev).

Abstract

The ultrafast carrier dynamics of GaAs(100) surfaces passivated with different sulfide solutions is studied by time-resolved measurements of infrared absorption using the femtosecond visible-pump infrared-probe technique. After passivation of n-GaAs(100) surface with the solution of ammonium sulfide in 2-propanol the three-fold decrease of the surface recombination velocity is observed. The treatment of the n-GaAs(100) surface with the aqueous sulfide solution has a smaller impact on the surface recombination velocity. The different effect of aqueous and alcoholic sulfide solutions on the efficiency of surface passivation is caused by the different mechanisms of charge transfer at the semiconductor/solution interfaces.

## 1. Introduction

Gallium arsenide (GaAs) is one of the most important III–V semiconductor materials and its high electron mobility and rather wide direct band gap make GaAs quite promising in designing high-speed electronic and optoelectronic devices. However, the GaAs(100) surface even prepared by molecular beam epitaxy exhibits a high density of states located near midgap resulting in Fermi level pinning and high surface recombination velocity [1]. With decreasing size of the active regions of semiconductor devices down to the nm range, the importance of controlling surface and interface properties increases. Marked improvement of the performance of the devices based on III–V compound semiconductors can be achieved by chemical treatment with aqueous sulfide solutions that remove the native-oxide layer and passivate semiconductor surface chemically and electronically. Sulfur passivation resulted in performance enhancement for different III–V bipolar [2,3] and field effect [4,5] transistors, solar cells [6], light-emitting and laser diodes [7–9], as well as photoelectrochemical processes [10]. The alternative approaches with using the non-aqueous solutions are of great interest for III–V surface passivation now. In particular, it was demonstrated that the alcoholic

sulfide solutions provide more effective electronic passivation of GaAs surface than the aqueous ones and offer a long-term stability of the electronic properties of the semiconductor/sulfide coat interface in ambient even under the influence of strong laser radiation [11]. Treatment with alcoholic sulfide solutions was used to improve performance of different lasers and optical amplifiers [12–15], as well as photodetectors [16]. This study is concerned with the investigations of the dynamics of the photogenerated carries in GaAs treated with various sulfide solutions focused on understanding the effect of surface chemical treatment on the recombination at GaAs(100) surface [17,18]. The studies were performed by femtosecond visible pump mid-infrared probe technique. This technique is most suitable for monitoring of the free carrier dynamics in semiconductor since the free carriers absorb infrared light [19].

## 2. Experimental

The samples used in the present study were made from n-GaAs(100) wafers doped to (3–5) × $10^{17}$ $cm^{-3}$. Before sulfur treatment the sample was etched with HCl for 100 s to remove the native oxide layer. Then the sample was cleaved to 3 pieces. One of them was not subjected to any further treatment and used as reference. The second and third samples were then treated with different sulfide solutions for 10 min. The solutions used were ammonium sulfide [$(NH_4)_2S$] in water ($H_2O$) and in 2-propanol (2-$C_3H_7OH$). The concentration of ammonium sulfide in aqueous and in alcoholic solution was 25% and 2–3% by volume, respectively. After the sulfur treatment the sample was rinsed with the respective solvent (water or 2-propanol) and dried in air. A femtosecond visible-pump infrared-probe system is described in detail elsewhere [20,21]. Briefly, a fs-pulse train generated by a Ti:sapphire regenerative amplifier system (Quantronics, 4812RGA/4823S/C) was used to pump two optical parametric generation/optical parametric amplification (OPA/OPG) systems (Light Conversion, TOPAS 8034). The probe beam (with the wavelength of 4 μm) was obtained by difference frequency

generation in an AgGaS2 crystal of signal and idler beams from an OPA/OPG sys-tem. The pump beam (790 nm, 1 μJ/pulse) was obtained by second harmonic generation in a BBO crystal of the signal beam from another OPA/OPG system. The probe beam was split into two beams: one for reference and the other for the sample. Both signals were monitored by InSb detectors (Hamamatsu, P5172-200). The pump and probe beams were non-collinearly focused and overlapped with each other on the sample surface with incident angles 25◦ and 0◦ (surface normal), respectively. Infrared signals were recorded by a personal computer as normalized absorption change, $\Delta OD = I_0 - I/I_0$, where $I_0$ and I represent the intensities of the infrared beam transmitted through the sample with and without visible excitation. The delay time between the pump and probe pulses was controlled by an optical delay line consisting of a retroreflector on a 1-axis translation stage (Sigma Koki) with 1 μm (3.3 fs) resolution and 1 ns maximum delay.

## 3. Results and discussion

The time-resolved normalized absorption decays for the reference (untreated) and sulfur-treated GaAs samples are shown in Fig. 1. At zero pump-probe delay time the absorption of the infrared probe radiation increases rapidly due to the free carrier absorption by the photogenerated electrons and holes. At early delay times surface recombination significantly depopulates the concentration of photogenerated carriers, while at later delay times (≥200 ps) the carriers have time to diffuse into the bulk reducing the role of surface recombination [22,23]. The absorption decay is very complex for all three samples under investigation. Thus, the non-exponential shape of the absorbance decay was simulated using a solution of the one-dimensional diffusion equation [22] in order to obtain the values for surface recombination velocity S. For all three samples a good agreement between simulation and experimental data was obtained in the initial segments of the decay curves (up to 100 ps) when the bulk lifetime $\tau_b$ = 8 ns taken from the limit of the decays in Fig. 1 was used (Fig. 2).

After 100 ps (for untreated sample and for the sample treated with the aqueous sulfide solution) and after 300 ps (for the sample treated with the alcoholic sulfide solution) the experimental absorbance curve was higher than the simulated one due to the presence of free carriers. Better agreement is achieved when the larger values of the bulk lifetime $\tau_b$ (of the order of a few microseconds) are used in simulations. For the untreated reference sample the best fit to the initial absorption decay was obtained when the surface recombination velocity value $S = 2 \times 10^5$ cm/s was used (Fig. 2). This value is in a good agreement with the data published previously for n-GaAs(100) with similar doping level [24–26]. For the n-GaAs(100) surfaces treated with aqueous ($(NH_4)_2S + H_2O$) and alcoholic ($(NH_4)_2S$ + 2-$C_3H_7OH$) sulfide solutions the surface recombination velocity decreases to $S = 1.25 \times 10^5$ cm/s and $S = 6 \times 10^4$ cm/s, respectively (Fig. 2). The data presented show that the recombination velocity at the n-GaAs(100) surface decreases after the treatment of the surface with the sulfide solutions and the solution of the ammonium sulfide in 2-propanol is more efficient than the aqueous sulfide solution. Moreover, the treatment with the aqueous sulfide solution has very little effect on surface recombination velocity in n-GaAs(100). These data are in a good agreement with the previous results of photoluminescence and Raman scattering study of n-GaAs(100) passivated with aqueous and alcoholic solutions of ammonium sulfide [27,28]. In particular, it was found that after the treatment of GaAs(100) surface with aqueous sulfide solution the photoluminescence intensity increases, whereas the surface depletion layer width that characterizes the density of the occupied surface states remains unchanged [28]. The little effect of the treatment with aqueous sulfide solution on the surface recombination velocity in n-GaAs(100) was observed also in [20]. On the other hand, the treatment of the GaAs(100) surface with the solution of ammonium sulfide in 2-propanol resulted in considerable increase in photoluminescence intensity and in essential decrease of the surface depletion layer depth (i.e. density of surface states) [28]. Moreover, in accordance with the results obtained by means of the Raman-scattering spectroscopy, the reduced surface

depletion layer depth on GaAs(100) surface treated with alcoholic sulfide solution remains unchanged after exposure in air within at least 2 months [29]. Different extent of modification of the electronic properties of the GaAs(100) surface can be explained in terms of the proposed model of interaction of the semiconductor surface with aqueous and alcoholic sulfide solutions. As soon as the sulfide solutions used in this study are almost neutral (in aqueous solution pH ~ 8), the main species adsorbed on semiconductor surface in the course of sulfide treatment from solutions are the $HS^-$ ions. Once these ions are in aqueous or in alcoholic solution, their chemical properties and reactivity are modified due to electrostatic interaction and formation of the hydrogen bonds with the polar solvent molecules. Therefore, the chemical properties of $HS^-$ ions in aqueous and in alcoholic solution will be principally different and the mechanism of interaction of such solvated ions with the semiconductor surface atoms should depend on the solvent. Besides, it was demonstrated that the presence of electron acceptors in the passivating sulfide solution is essential for electronic passivation of semiconductor surface [30]. In accordance with density functional theory calculations, the hydrated $HS^-$ ions (solvated by water molecules) have equal probability to donate and to accept electrons in the course of chemical reaction, whereas the water molecules forming the hydration shells around the $HS^-$ ions can neither accept nor donate electrons [31,32]. Therefore, on interaction of the semiconductor surface with aqueous sulfide solution the charge localized in the surface states can be transferred only to sulfur atoms of $HS^-$ ions, which after adsorption remains on the surface (Fig 3a). So, the charge localized in the surface states remains intact. Some reduction of the surface recombination velocity in this case can be associated with the shift of the energy level of the surface state due to chemical interaction of this state with the hydrated $HS^-$ ion. By contrast, the $HS^-$ ions solvated by alcohol molecules can easily donate electrons but hardly accept them, while the alcohol molecules of the solvation shell can easily accept electrons [30,31]. Therefore, the alcohol molecules from the solvation shell can act as electronic acceptors and charge from the semiconductor surface

states can be transferred to solvent molecules and will remain in the solution or go further to the gas phase (Fig. 3b). As a result, the density of occupied surface states decreases and the reduction of the surface recombination velocity will be more essential than in the case of the treatment of semiconductor surface with the aqueous sulfide solution.

## 4. Conclusions

Femtosecond time-resolved visible pump infrared probe absorption spectroscopy was used to study the effect of surface treatment on the dynamics of photogenerated carriers in n-GaAs(100). It was shown that the treatment with the sulfide solutions results in the decrease in the surface recombination velocity. The reduction of the surface recombination velocity depends on the solvent from which the sulfur adsorption proceeded. After the treatment of the GaAs(100) surface with the solution of ammonium sulfide in 2-propanol the surface recombination velocity decreases by a factor of three. The effect of the treatment with the aqueous sulfide solution is less significant. The different effects of various sulfide solutions on the efficiency of surface passivation are caused by the different mechanisms of interaction of $HS^-$ ions with the semiconductor surface in aqueous and alcoholic sulfide solutions.

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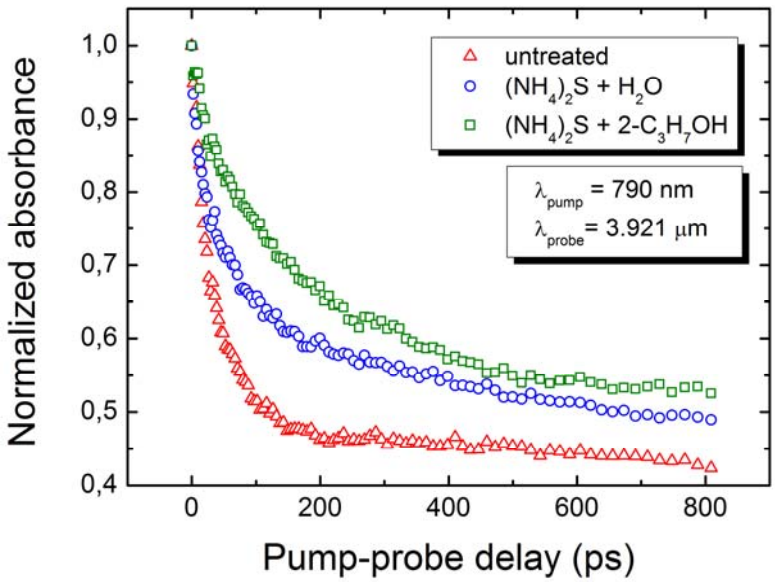


Fig. 1. Normalized time-resolved absorbance decay for untreated n-GaAs(100) sample, as well as for samples passivated with aqueous and alcoholic sulfide solutions as measured with femtosecond visible pump infrared probe technique.

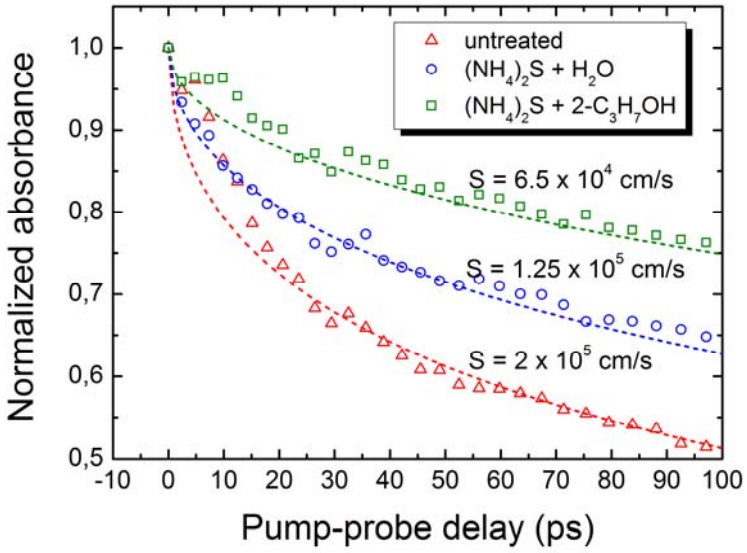


Fig. 2. Fitting of the initial absorbance decay for untreated n-GaAs(100) sample, as well as for samples passivated with aqueous and alcoholic sulfide solutions. Dots represent experimental data and dashed lines indicate fitting results obtained using a solution of the one-dimensional diffusion equation from Ref. [22].

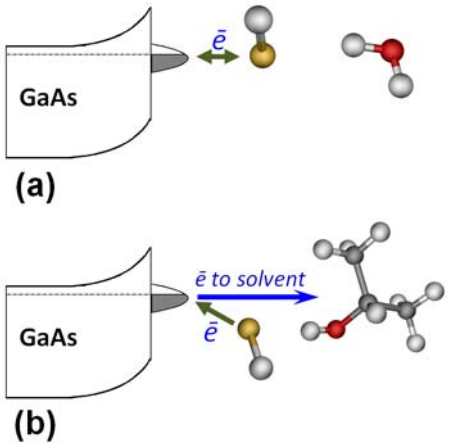


Fig. 3. Scheme of the interaction of the $HS^-$ ion in aqueous (a) and in alcoholic sulfide solution (b) with the acceptor states at n-GaAs(100) surface.