Femtosecond Visible Pump Mid-IR Probe Study on the Effects of Surface Treatments on Ultrafast Photogenerated Carrier Dynamics in n-GaAs (100) Crystals

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The femtosecond visible pump mid-IR probe technique was employed to investigate photogenerated carrier dynamics in n-GaAs (100) crystals subjected to various surface treatments in a time domain of picoseconds–several tens of picoseconds. Pt- or Ru-treatment significantly accelerated the carrier recombination as a result of the introduction of surface states. The recombination rate was also increased by Au-treatment but less significantly than that by the Pt- or Ru-treatment. The effect of sulfide treatment on the recombination dynamics seemed to be rather small, although it has been reported that the density of surface states is decreased by the sulfide treatment.

Control of the position and density of electronic states localized at the surafce of semiconductors, i.e., surface states, is not only an important subject in fundamental surface science but also one of the critical issues in device applications since electronic properties are greatly dependent on the nature of surface states.[1]

GaAs is considered to be one of the most important semiconductor materials for high-speed electronic and optoelectronic devices but is also known to possess a high density of surface states, which prevents the wide use of GaAs in electronic devices. It was found that surface-state density was significantly reduced and, therefore, the device performance was improved by chemical treatment of the GaAs surface with, for example, ammonium sulfide.[2–10]

Surface treatment also strongly affects the photoelectrochemical properties of semiconductor electrodes.[11] For example, Heller et al. demonstrated that the performance of a wet-solar cell was drastically improved by treating the surface with Ru or Pt and suggested that the improvement was caused by the decrease of surface-state density within the energy gap.[12] On the other hand, we have shown that the dark current and photocurrent, both due to hydrogen evolution reaction (HER), were increased and decreased, respectively, by Ru- or Pt-treatment of a p-GaAs electrode surface, and suggested that the deposited metal acted as catalyst for HER as well as a recombination center of the photoexcited carriers.[13,14] Improvement in photoelectrochemical characteristics due to the reduction of the surface-state density by the treatments with sulfide[15] and Au[16] has been also reported.

Effects of surface treatments have been investigated using various techniques, including electrochemical impedance spectroscopy and photoluminescence (PL).[13,14] Although these studies provided evidence of the introduction of surface states as well as information on the position and density of surface states, the information on the dynamics of photogenerated free carriers, i.e., electrons, and holes, within the semiconductor is essential to clarify the effect of surface treatment on optical, electronic, and photoelectrochemical properties. The relaxation mechanisms of photogenerated carriers in GaAs have been investigated in sub-ps–ps time domain[17] mostly in a visible light region using visible-pump visible-probe[18] and fluorescence up-conversion methods.[19] The visible-pump IR-probe technique is the most suitable technique for directly monitoring free carrier dynamics in a semiconductor because free carriers in a semiconductor absorb IR light.[20] In the present study, the femtosecond visible-pump IR-probe technique was employed to investigate the effects of various chemical treatments on carrier recombination dynamics in n-GaAs (100).

Si-doped n-GaAs (100) wafers (doping density: 8–30 $\times$ 10^{18} cm^{-3}, Mitsubishi Chemicals), one side of which was mirror polished, were used as samples. Au treatment was achieved by vacuum deposition of an approximately 10-nm-thick Au layer on the GaAs sample (ULVAC, EBH-6). Sulfide (S-), Ru, and Pt treatments were carried out by immersing the GaAs sample in $(NH_4)_2S_x$ solution for 24 h,[15] in 0.1 M HNO_3 + 0.01 M anhydrous $RuCl_3$ solution for 2 min,[13] and in 20 mM H_2PtCl_6 solution for 15 s,[14] respectively, and then rinsed with Milli-Q water.

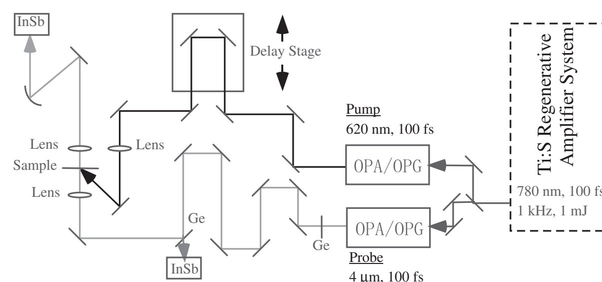

Figure 1. Schematic diagram of the femtosecond visible-pump IR-probe system.

A femtosecond visible-pump IR-probe system is schematically shown in Figure 1. The details of the system will be described elsewhere.[21] Briefly, an 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 (Quantronics, TOPAS 8034). The probe beam (4 μm, 0.03–0.1 μJ $pulse^{-1}$) was obtained by difference frequency generation in an $AgGaSe_2$ crystal of signal and idler beams from an OPG/OPA, and the pump beam (620 nm, 0.5–3.0 μJ $pulse^{-1}$) was obtained by second harmonic generation in a BBO crystal of the signal beam from another OPG/OPA. The probe beam was split into two, one for reference and the other for the sample. Both signals were detected by InSb detectors (Hamamatsu, P5172-200). The incident angles of the visible pump and IR-probe beams were 25° and 0°, respectively. IR signals were recorded by a personal computer as noramlized absorption change, $\Delta OD = I_0 - I/I_0$, where I_0 and I represent the intensities of the transmitted IR beam with and without visible excitation, respectively. Both I and I_0

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were normalized by the reference IR beam intensity within a given fluctuation, which was typically ±5%.

The ability of the present system to perform the time-resolved IR absorption measurement was confirmed by measuring the photogenerated carrier dynamics in as-received n-Si (100) and n-GaAs (100) wafers. In both cases, the IR absorption instantaneously increased with visible excitation and, faster decay of the ΔOD was observed in the GaAs sample than in the Si sample, as was previously reported for the photogenerated carrier dynamics in p-Si (100) and GaAs (100).[22] Thus, it was considered that the visible-pump IR-probe system used in the present study could be used to estimate the effect of surface treatment on free carrier dynamics in a ps time domain for various GaAs samples.

Figure 2 shows the time-resolved transient IR absorption changes observed for bare, i.e., etched, and surface-treated n-GaAs (100) wafers.[23] The absorption change is normalized to the maximum of the absorption change at $t = 0$. It is clear that the decay rate was increased by the Pt-, Ru-, and Au-treatment but was not affected or even decreased by the S-treatment. The increase in the absorption decay rate by the metal treatments shows that the recombination of photogenerated carriers on the GaAs surface is accelerated by transition-metal treatment of the GaAs surface as we previously suggested[13,14] in contrast to the results of Heller et al.[12] This clearly shows that surface states, which act as a recombination center, are introduced by the metal treatment.[13,14] The decay in the Au-treated GaAs was faster than that in the bare and S-treated samples, but slower than in the Ru- and Pt-treated samples. There are at least two reasons for this difference. One is the physical nature of the metal deposit. While Au was physically deposited, resulting in the formation of a homogeneous Au layer on the GaAs surface, Pt and Ru were chemically deposited, resulting in site-selective formation of metal nanoparticles on the surface. The formation of a relatively homogeneous Au island film can result in the formation of Schottky junction at the Au/GaAs interface, and the band bending at the Au/GaAs interface is, therefore, expected to be significantly different from that at the Ru/GaAs or the Pt/GaAs interface. The other reason is the electronic character of the modified metal itself. When a Au film was vacuum evaporated on GaAs, new compounds such as Au_3Ga and Au_7Ga_2 are reported to be formed.[24] This may make the evaporated Au film a less effective recombination center than Ru or Pt.

The decay rate was not greatly affected by the S-treatment,

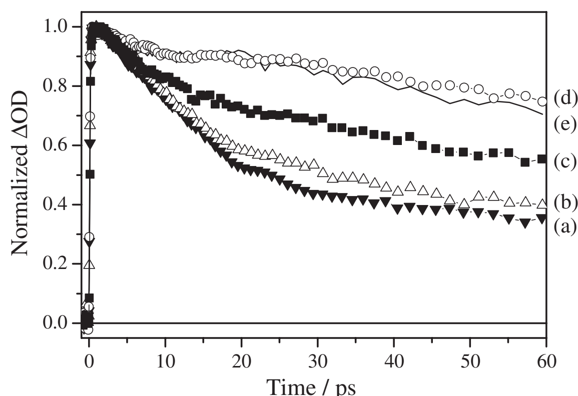

Figure 2. Normalized transient absorption changes at (a) Pt- (▼), (b) Ru- (△), (c) Au- (■), (d) S- (open circle) treated and (e) bare (solid line) GaAs samples.

although there seemed to be a slight decrease in the decay rate, in contrast to the previously reported findings of the removal of surface states by the S-treatment.[15,25–27] More detailed examination for the effects of the S-treatment may be required.

In summary, femtosecond time-resolved visible-pump mid-IR-probe measurement was shown to be very useful for studying the effects of surface treatments on the photogenerated carrier dynamics in GaAs (100) single crystals. The surface treatments affected the recombination dynamics of photogenerated carriers in the time domain of ps to several tens of ps. The Pt- or Ru-treatment significantly accelerated the carrier recombination as a result of the introduction of the surface states. The recombination rate was also increased by the Au-treatment but less significantly than by the Pt- or Ru-treatment. The effect of the S-treatment on the recombination dynamics within the time domain of the present study seemed to be rather small, although it has been reported that the density of surface states is decreased by the sulfide treatment.

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