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Carrier recombination velocities at the SiO₂/Si interface investigated by a photo-thermal reflection microscopy

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Abstract

Photo-thermal reflection microscopy has been used for investigating semiconductor materials to evaluate carrier diffusivity, lifetime and surface recombination velocity. We developed this technique to obtain carrier recombination velocities at the interface between SiO_2 oxide film and Si substrate. Two samples with different oxide film thickness of 92 and 45 nm were prepared. Since the oxide film layer does not absorb the pump and probe laser light, carrier recombination velocity at the SiO_2/Si interface can be estimated. Curve fitting procedures with the theoretical prediction results in an estimation of the interface recombination velocity of 100 cm/s for thick oxide sample. When the sample was chemically etched, the recombination velocity increases to 2500 cm/s. The chemical etching results in the drastic increase of the recombination velocity. The etching solution may soak through the SiO_2 oxide film layer and attack the Si surface during the chemical etching. Increase of the number of the interface traps induces the increase of the carrier recombination velocity at the interface. We, therefore, found that the present photo-thermal reflection (PTR) microscopy is a useful technique for investigating the carrier dynamics at SiO_2/Si interface.

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1. Introduction

Recent demand for drastic decreasing of an active area and a thickness in the metal-oxide-semiconductor (MOS) structure requires an improvement of the quality of both the oxide film itself and the interface with the substrate. This is because the $\mathrm{SiO}_2/\mathrm{Si}$ interface plays a dominant role when the oxide thickness becomes smaller. Recent technological development for Si epitaxial layers provides for increased reliability of semiconductor device and ultimately more functional integrated circuit devices [1]. Although controls over surface reaction during the thermal oxidation become important, no experimental methodology has been available for making clear the growth mechanism of the oxide layers until now. It, then, becomes important to characterize the interface between the layer and substrate in more detail.

Modulated photo-reflectance is a non-contact and non-destructive characterization technique of semiconductors.

Among those techniques, photo-thermal reflection (PTR) microscopy has been used for investigating semiconductor materials to evaluate carrier diffusivity, bulk lifetime and surface recombination velocity [2–4]. Since the observed signal strongly depended on the surface recombination velocity, surface change induced by an ion implantation has been well characterized by this technique [5]. In this paper, we report on the estimated carrier recombination velocity of SiO₂ and Si interface for thick SiO₂ films grown on the substrate by using our methodology from the photo-thermal phenomena points of view.

We show that chemical etching strongly affects the interface properties even for the case that thick SiO₂, more than 50 nm, covers the Si surface.

2. Principles of the photo-thermal microscopy

When the sample surface is illuminated by a laser light, photogenerated free carriers diffuse along and parallel to the direction of sample thickness and recombine in the bulk and at the surface [2]. The excess carrier concentration n(r, t) in the sample is determined by solving carrier diffusion equation, with appro-

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priate boundary conditions at the surface, as

$$\frac{\partial n}{\partial t} = D_{\rm e} \nabla^2 n - \frac{n}{\tau} + \Phi,\tag{1}$$

where $D_{\rm e}$, τ and Φ are electron diffusivity, carrier lifetime and incident photon flux, respectively. Surface recombination velocity $v_{\rm r}$, which induce drastic change to the carrier dynamics, are taken into account for the boundary conditions. The quantum efficiency is supposed to be one for simplicity. Temperature rise T(r,t) in the sample under the light illumination at the photon energy hv larger than that of band gap energy, $E_{\rm g}$, is calculated by solving thermal diffusion equation given below,

$$\frac{\partial T}{\partial t} = D_{\rm T} \nabla^2 T + \frac{h \nu - E_{\rm g}}{\rho C} \Phi + \frac{E_{\rm g}}{\rho C} \frac{n}{\tau},\tag{2}$$

where $D_{\rm T}$, ρ , C are thermal diffusivity, density and specific heat of semiconductor sample, respectively. The heat source for this equation arises from the following two mechanisms. First is due to the fast carrier non-radiative relaxation to the conduction band minimum or valence band maximum. The energy of $(h\nu - E_{\rm g})$ is dissipated in this case (second term of Eq. (2)). Second is the non-radiative recombination of the free carriers diffused throughout the sample with energy $E_{\rm g}$ (third term).

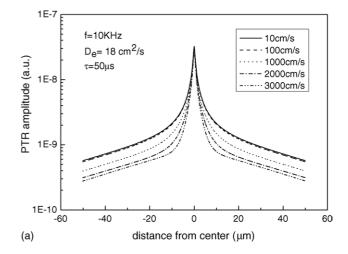
Photo-thermal reflection microscopy detects the change of the surface reflectivity in terms of refractive index change modulated by the light illumination. Photo generated free carriers diffuse in the sample until they recombine through non-radiative transition. Therefore, the dynamics of free carriers play an important role in temperature rise through the sample and at the surface followed by the modulation of the reflectivity. Modulated free carrier density contributes directly to the modulation of the reflectivity through Drude effect.

Therefore, relative reflectivity change at the surface is, then, calculated by [4]

$$\frac{\Delta R}{R} = \frac{1}{R} \frac{\partial R}{\partial T} \Delta T + \frac{1}{R} \frac{\partial R}{\partial n} \Delta n. \tag{3}$$

Since Eqs. (1) and (2) determine the distribution of photogenerated carriers and the temperature rise as a function of a distance from the illuminated spot on the surface, the expected spatial distribution of the reflectivity change is calculated [2].

We considered that the carrier recombination velocity v_r at the interface between SiO₂ film and Si substrate was the most important parameters for understanding the observed experimental results. As discussed later, since the light cannot be absorbed in SiO₂ film layer, we consider the surface recombination velocity v_r in Si should be a carrier recombination velocity at SiO₂/Si interface. Accordingly, the effect of the substrate (Si) surface recombination velocity on the PTR results in Eq. (3) is first discussed here. Fig. 1 shows the calculated PTR signal amplitude (a) and phase (b) for different v_r as a parameter. Horizontal axes are taken for the distance between the pump and probe laser beam. Electron diffusivity D_e and the lifetime of the carrier τ are supposed to be $18 \text{ cm}^2/\text{s}$ and $50 \mu \text{s}$ as in the case for typical Si bulk sample [3]. The modulation frequency f was set at 10 kHz. For higher modulation frequencies, observed change in the calculated PTR curves as a function of v_r becomes small.



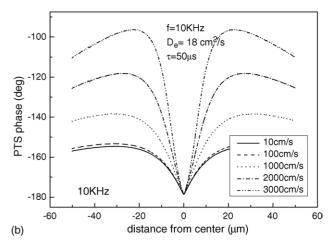


Fig. 1. Theoretical calculation of the photo-thermal reflection (PTR) amplitude (a) and phase signal (b) as a function of the distance between pump and probe beam

Figures show that the change for the phase signal is more drastic than the amplitude signal. We, therefore, discuss the phase change for the calculated and experimental results. When $v_{\rm r}$ decreases from 3000 to $10\,{\rm cm^2/s}$, phase changes from -100 to -160° around a distance at $20\,\mu{\rm m}$. Since the carriers can diffuse far from the illuminating spot when the recombination velocity decreases, the phase signal remains around -160° for $v_{\rm r}=100\,{\rm cm^2/s}$. No significant effect in the phase signal could be observed below $100\,{\rm cm^2/s}$. Surface recombination velocity may be controlled by the presence of the traps underneath the native oxides on Si substrate. We have also discussed the PTR phase by changing the other physical parameters such as $D_{\rm e}$, τ and fraction of the thermal/plasma components. Details are discussed in the following section.

3. Experimental

Reflectivity change due to photo-excitation by Ar^+ ion laser of 514 nm as a pump beam was measured as a photo-thermal reflection signal from the sample surface as a function of the distance from the illumination spot. The reflectivity was measured by a probing laser diode of 670 nm. Both laser beams of

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