

## Rapid Thermal Annealing Using the Combustion of $H_2$ with $N_2O$

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The combustion of  $H_2$  gas with  $N_2O$  gas was investigated in order to rapidly heat substrate to a high temperature. A transient thermometry with a 100 nm-thick Cr film as a temperature sensor formed on quartz substrate was used to measure temperature change at the surface. The gas combustion was induced by heating a W filament. It propagated with a velocity larger than 100 m/s throughout a chamber for an initial total gas pressure of 500 Torr ( $[H_2]/[N_2O]=1$ ). The sample surface is heated to 800 °C for a substrate temperature of 300 °C. The full heating time width at half maximum was 5 ms.

### 1. Introduction

Rapid thermal annealing has been important to device fabrication technology because a total required energy for heating treatment must be reduced for fabrication of large scale integrated circuits with a high packing density and a high yield. The rapid thermal annealing is also attractive for low temperature fabrication of thin film transistors on glass substrates with no heat resistivity. Infrared (IR) rapid thermal annealing has realized a heating treatment up to 1100 °C for a few seconds.<sup>1,2)</sup> It activates ion-implanted species well. However, there are still a problem of unwanted impurity diffusion during the heating treatment. Pulsed laser heating has been also widely studied for surface treatment. The sample surface is heated very rapidly and melted shorter than 1  $\mu$ s. Several surface modifications, for example, crystallization, activation of implanted species and doping, are possible.<sup>3-5)</sup> However, it is not yet easy to apply the laser treatment to fabrication processing because of inhomogeneous beam intensity and intensity fluctuation. Moreover, the high heating and cooling ratio ( $10^8 \sim 10^{10}$  K/s) may cause a stress-induced defects.

This paper reports a rapid annealing method using a gas reaction energy, which is produced by burning hydrogen gas with  $N_2O$  gas, via the following reaction,  $H_2 + N_2O \rightarrow H_2O + N_2$ . Here, the combustion reaction energy is 324 kJ/mole.<sup>6)</sup> The reaction energy is used to heat a sample rapidly. The paper characterizes the heating and cooling properties at the surface of quartz substrates using a transient thermometry with a Cr film as a temperature sensor.<sup>7)</sup> A combination of the present rapid heating method with the preheating of substrate to obtain a higher surface temperature is also reported.

### 2. Experimental

Two Cr wires with a thickness of 100 nm, a width of 0.2 mm and a length of 10 mm were formed with an interval of 25 mm on a 1 mm-thick quartz glass substrate. They were connected to electrodes inside a chamber with a volume of 7

liters. The initial temperature of the sample before the gas reaction was controlled at room temperature as well as at 300 °C by a current heater. After the chamber was evacuated,  $H_2$  and  $N_2O$  gases were introduced to the chamber with a same partial pressure respectively ( $[H_2]/[N_2O]=1$ ). A W filament installed at a chamber wall was heated to initiate the gas combustion. Because the gas combustion increases the gas temperature and results in a higher gas pressure, the chamber had a pressure-proof structure to 10 bars. Change in the resistivity of the Cr wires were measured by a digital storage oscilloscope during and after the gas reaction.

### 3. Results and discussion

Figure 1 shows the changes in temperature of the Cr wires as a function of time for an initial total gas pressure of 440 Torr and the substrate temperature of room temperature. The temperature was calibrated from a relation between the resistivity of the Cr wires and the temperature which was carefully measured using a furnace before the gas combustion experiments. The temperature was increased rapidly by the gas combustion and reached 450 °C at maximum within 2 ms. Then it decreased gradually according to heat diffusion into the substrate. The full width at the half maximum was 5 ms. The result of Fig.1 shows that the gas reaction energy is effectively transferred to the sample. Figure 2 shows the maximum temperature heated by the present gas combustion as a function of the initial total gas pressure for the initial substrate temperatures at room temperature and at 300 °C, respectively. Figure 2 also shows the velocity of the combustion propagation, which was obtained from the retardation of the temperature change between the two Cr wires with the 25 mm interval. The maximum temperature increased as the total gas pressure increased for both substrate temperatures. Especially for the substrate temperature at 300 °C, the temperature reached 800 °C at the initial total gas pressure of 500 Torr. The propagation velocity of the gas combustion increased as the total gas pressure increased as shown in Fig.2. It is higher than 100 m/s for 500 Torr.

The present heating method was applied to activation of

dopant species in semiconductor. 0.2%-phosphorus-doped hydrogenated amorphous silicon (a-Si:H, P(0.2%)) films with a thickness of 10 nm were heated by the gas combustion with the initial total gas pressure of 500 Torr and the initial substrate temperatures at room temperature and at 330 °C, respectively. The electrical conductivity was increased from  $2 \times 10^{-6}$  S/cm to  $2 \times 10^{-3}$  S/cm by the treatment at 330 °C-initial substrate temperature, while it hardly changed for the case of the initial substrate temperature at room temperature, as shown in Fig.3. The result of Fig.3 shows that this heating treatment can give the samples an energy to activate dopant species in the films.

The experimental results of Figs.1-3 reveal that the gas combustion has a possibility of millisecond-order heating treatment. The combustion, which is initiated with help of the heated W filament, produces hot gas molecules because of the high reaction energy. They heat adjacent gases so that they successively cause another reactions (chain reaction)<sup>8)</sup>, which result in the propagation throughout the chamber. The maximum heating temperature can be controlled by the initial gas pressure as well as the preheating temperature. The heating treatment over a large area can be realized via the propagation of the combustion throughout the chamber. The present heating method can be useful for activation of dopant species in semiconductor and ohmic contact between semiconductor and metal. This method may be also useful for rapid annealing treatment of some ceramic films because very hot and oxidized gas molecules (H<sub>2</sub>O) are produced during the combustion.

#### 4. Summary

The, the gas combustion of H<sub>2</sub> with N<sub>2</sub>O was investigated for a rapid thermal treatment. 100 nm-thick Cr films were used to measure the temperature at the surface of quartz substrate. The gas combustion induced by heated W filament propagated throughout the chamber. The propagation velocity increased above 100 m/s as the initial total gas pressure increased to 500 Torr ([H<sub>2</sub>]/[N<sub>2</sub>O]=1). The sample surface was rapidly heated and reached a maximum temperature within 2 ms. The full time width at half maximum was 5 ms. The maximum temperature increased to 500 °C, when the initial total gas pressure increased to 500 Torr. The preheating of the sample to 300 °C helped the sample surface to be heated 800 °C. The electrical conductivity of 10 nm-thick a-Si:H,P(0.2%) was increased from  $2 \times 10^{-6}$  S/cm to  $2 \times 10^{-3}$  S/cm by the treatment with the initial total gas pressure of 500 Torr at 330 °C-initial substrate temperature. These results show that the present method has a possibility of millisecond-order rapid thermal treatment.

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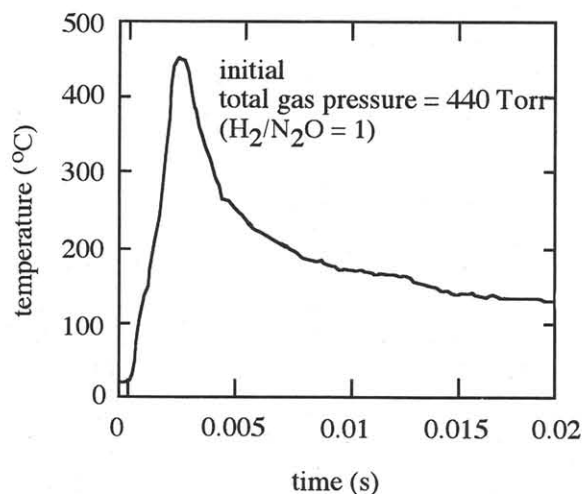


Fig.1. Temperature change at the quartz surface during and after the gas combustion for the initial total gas pressure of 440 Torr ( $[H_2]/[N_2O]=1$ ).

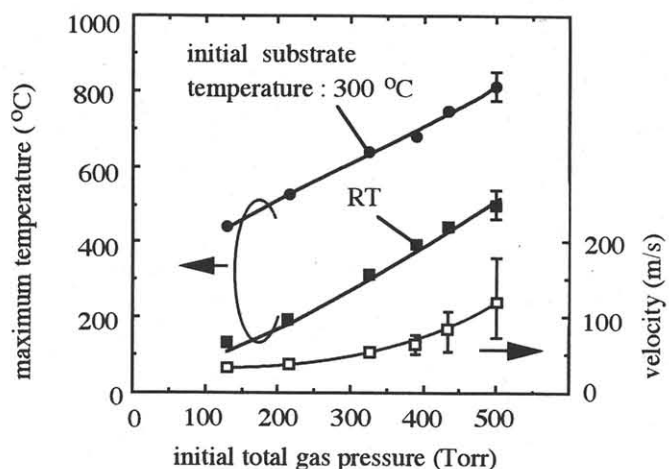


Fig.2. Maximum temperature as a function of the initial total gas pressure for the initial substrate temperature at the room temperature and 300 °C, respectively. The velocity of the combustion propagation as a function of the initial total gas pressure is also shown. It was obtained from the retardation of the temperature change between the two Cr wires with the 25 mm interval.

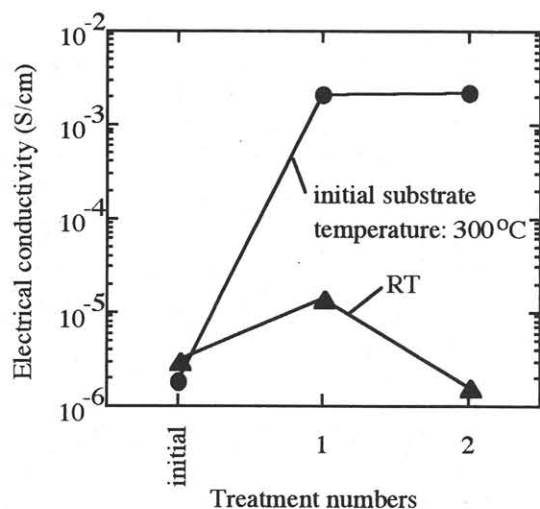


Fig.3. Electrical conductivity of the 0.2%-phosphorus-doped hydrogenated amorphous silicon films with a thickness of 10 nm as a function of the treatment numbers for the initial total gas pressure of 500 Torr and the initial substrate temperatures at room temperature and at 330 °C, respectively.