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The Gas Combustion of H_2 with N_2O Used for Rapid Thermal Annealing

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The gas combustion of H_2 with N_2O was investigated to develop a rapid thermal annealing method. Spectra of the light emission caused by the combustion show a gray body irradiation characteristic with a gas temperature of 2200 K with an initial total gas pressure of 500 Torr ($[H_2]/[N_2O] = 1$). A transient thermometry with a 100-nm-thick Cr film as a temperature sensor formed on a quartz substrate was used to measure temperature changes at the surface during and after combustion. Heating to 800°C was achieved within 2 ms using a substrate preheated to 300°C. The increase of electrical conductivity was achieved from 4×10^{-7} S/cm to 7×10^{-4} S/cm by the combustion for 0.5% phosphorus-doped amorphous silicon films.

KEYWORDS: rapid thermal annealing, black body radiation, transient thermometry, activation

1. Introduction

Rapid thermal annealing has been widely investigated for electrical device fabrication because the total required energy for the heating treatment must be reduced for fabrication of large-scale integrated circuits with a high packing density. Rapid thermal annealing is also attractive for low temperature fabrication of thin-film transistors on glass substrates. Infrared (IR)-lamp rapid thermal annealing (IR-RTA) has been used for heating treatment up to 1100°C for ~10 s.[1,2] IR-RTA activates ion-implanted-dopant species well. However, there is still the 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 for less than 1 μs. Several surface modifications, for example, crystallization, activation of implanted dopant species and doping, are possible using this treatment.[3–5] However, at this time, it is difficult to apply laser heating to fabrication processing because of the inhomogeneous beam intensity and intensity fluctuation. Moreover, the high heating and cooling ratio (10^8–10^{10} K/s) may cause stress-induced defects. We have recently reported a heating method using gas combustion of H_2 with N_2O,[6,7] which has the possibility of heating the sample for a few milliseconds over a large area.

This paper characterizes the gas combustion of H_2 with N_2O and the sample heating properties of this treatment. Gas temperature is analyzed by measuring light emission spectra during combustion. Transient thermometry with Cr film as a temperature sensor[8] is used to measure heating and cooling properties at the surface of the quartz substrates. The activation of dopant species is demonstrated for phosphorus-doped silicon films.

2. Experimental

Figure 1 shows a schematic of the apparatus for the gas combustion and the measurement system. A chamber with a pressure-proof structure up to 10 bar was built. It had a diameter of 25 cm and a volume of 7 L. A W filament was installed at the chamber wall to initiate the gas reaction. There was a quartz window for optical measurements. A spectrometer with a detector of an avalanche-photo diode was placed in front of the window to measure spectra of the radiation caused by the combustion between 650 nm and 900 nm. The output signals from the photo detector were measured by a digital storage oscilloscope during and after the gas reaction. The initial temperature of the sample placed on a sample holder was controlled by a resistance heater from room temperature to 300 °C. In order to measure temperature changes at a sample surface, two Cr wires with a thickness of 100 nm, a width of 0.2 mm and a length of 10 mm at the middle region were formed at

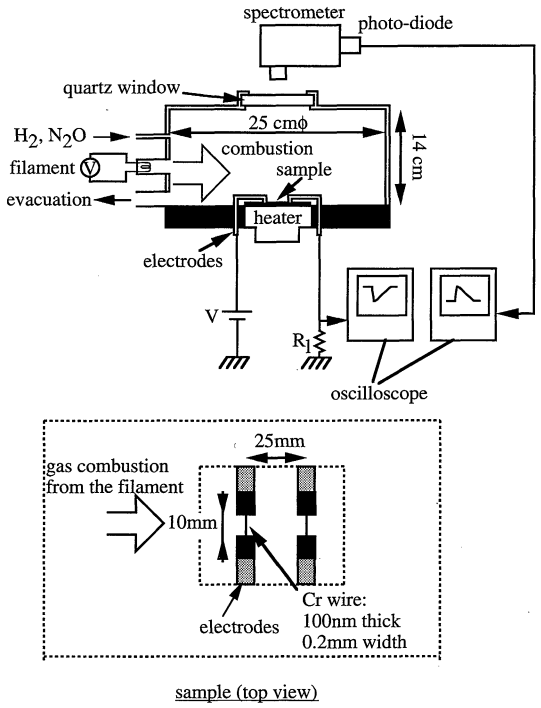

Fig. 1. Schematic of the apparatus used for the combustion of H_2 with N_2O. The chamber with a diameter of 25 cm has an evacuation line, a gas inlet, a W filament, a quartz window and electrodes for the temperature measurements using two Cr temperature sensors formed on a quartz glass substrate with a diameter of 4 inches. A spectrometer with an avalanche photo diode was placed above the quartz window. The Cr sensors were placed in the normal direction to the filament to measure the velocity of combustion propagation.

intervals of 25 mm on a 1-mm-thick quartz glass substrate of 4 inches in diameter. The sample was placed so that the Cr wires were lined in the normal direction to the filament in order to measure the time difference of the heating characteristics due to the propagation velocity of the gas combustion, as shown in Fig. 1. The Cr wires were connected to electrodes inside the chamber. A voltage was applied to the electrode. Changes in the resistivity of the Cr wires caused by the gas combustion were measured through changes in voltage crossing the load resistance connected to the electrode, as shown in Fig. 1. The chamber was evacuated by opening a valve connected to an evacuation system. After closing the valves, H_2 and N_2O gases were introduced to the chamber with the same partial pressure ($[H_2]/[N_2O] = 1$) using a gas delivery system via a gas valve. For investigating activation of the dopant species, a 0.5%-phosphorus-doped amorphous-silicon film with a thickness of 10 nm formed on a quartz substrate was heated to an initial substrate temperature of 300°C.

3. Results and Discussion

The combustion is initiated at the heated W filament. The burning of H_2 gas with N_2O gas via the following reaction, $H_2 + N_2O \rightarrow H_2O + N_2$, produces a large reaction energy of 324 kJ/mol.[9] The reaction produces hot gas molecules, which heat adjacent gases and propagates reactions successively so that combustion moves throughout the chamber. The photo diode detected the light emission produced from the combustion crossing the view point. Figure 2 shows the spectra of the maximum emission intensity in time evolution for the initial gas pressures, 300 Torr, 400 Torr and 500 Torr. The intensity increased monotonously as the wavelength increased for the each initial gas pressure. The intensity increased as the initial gas pressure increased for any wavelength. We assume that there are many enough collisions and energy exchange among the reacted hot gases so that the gas molecules irradiate light emissions according to the gray body radiation with an emissivity (< 1). The gas temperature was estimated by fitting spectra calculated with Planck's radiation equation, $I = 8\pi hc\lambda^{-5}\{\exp(hc/\lambda kT) - 1\}^{-1}$, to the measured spectra, as shown in Fig. 2. In the equation, h is Planck's constant, c is the light velocity, λ is the wavelength, k is the Boltzmann's constant and T is temperature. The increase of the emission intensity with increasing initial gas pressure means that the reacted hot gas has a higher temperature for a higher initial gas pressure. The maximum gas temperature increased from 1750 K to 2200 K as the initial gas pressure increased from 300 Torr to 500 Torr.

Figure 3 shows changes in the gas temperature as a function of time, which were obtained with changes in the radiation intensity at a wavelength of 900 nm and using the peak temperatures given in Fig. 2, for the combustion at the initial gas pressures of 300 Torr, 400 Torr and 500 Torr. Estimation of the temperature was carried out on the assumption that the gas had a constant radiation emissivity for each initial gas pressure case. Temperature rapidly increased and reached the maximum, and then decreased gradually for each combustion case. The

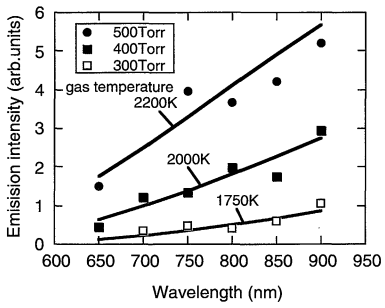

Fig. 2. Spectra of emission intensity at maximum for initial gas pressures, 300 Torr, 400 Torr and 500 Torr. Solid curves present calculated spectra using the black body radiation theory with temperatures shown in the figure.

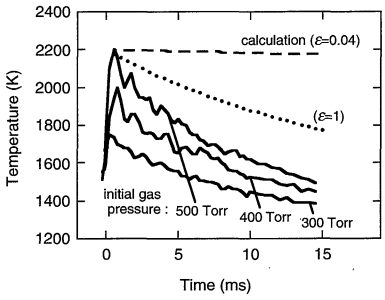

Fig. 3. Changes in temperature during and after combustion estimated by changes in the light emission for initial gas pressures, 300 Torr, 400 Torr and 500 Torr. Dashed curve gives the temperature change when the thermal energy is only released by radiation with an emissivity of 0.04 from the maximum temperature of 2200 K. Dotted curve presents the black body radiation case with the emmisivity of 1.

quenching rate was $\sim 9.2 \times 10^4$ K/s at the initial state for the 500 Torr-combustion and decreased to $\sim 4.7 \times 10^4$ K/s as the initial gas pressure decreased to 300 Torr. There are many paths for heat dissipation to take from the reacted hot gas. When only the energy loss via radiation is considered, the temperature decreases according to the equation, $dT/dt = -\epsilon S\sigma T^4 C^{-1} M^{-1}$, if the fourth power of the surrounding temperature $(T_{\text{surrounding}})^4$ is much lower than that of the gas temperature. σ is Stefan-Boltzmann constant, ϵ is the emissivity of the gas, whose value is estimated at $\sim$0.04 [10] for gas at 2200 K and at 5 bar $\{\sim (2200\,\text{K} \times 500\,\text{Torr})/(300\,\text{K} \times 760\,\text{Torr})\}$ in this experimental condition. S is the effective surface area from which the photo emission is irradiated, was 0.2 m^2. C is the specific heat of H_2O and N_2 mixed gases, which is 1.054 J/Kg.[11] M is the total weight of the mixed gas. Change in the temperature caused by the energy loss via radiation was plotted by the dashed curve in Fig. 3 for an initial temperature of 2200 K. The calculated temperature decreased much more slowly with time than the temperature obtained from the experimental results. Figure 3 also shows the calculated temperature change for the black body radiation case with the emissivity of 1 with a dotted curve. The gas temperature obtained experimentally decreased more rapidly than both calculated temperatures, as shown in Fig. 3, which indicates that the thermal energy of the reacted gas is primarily

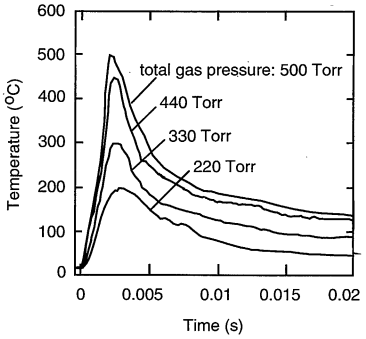

Fig. 4. Temperature changes at the quartz surface during and after the gas combustion for different initial total gas pressures ($[H_2]/[N_2O] = 1$).

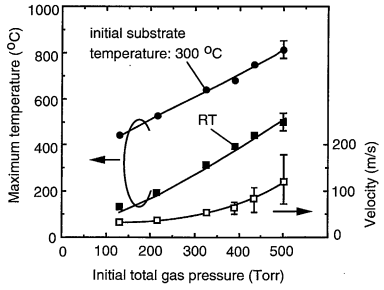

Fig. 5. Maximum temperature as a function of the initial total gas pressure for the initial substrate temperature at room temperature and at 300°C. The velocity of the combustion propagation as a function of the initial total gas pressure is also shown. It was obtained from the retardation of the temperature changes between two Cr wires placed at 25 mm intervals.

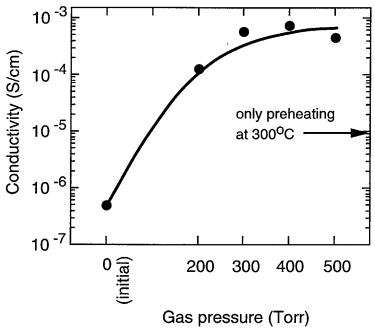

Fig. 6. Change in the electrical conductivity as a function of initial gas pressure with a substrate temperature of 300°C for 0.5%-phosphorus-doped 10-nm-thick silicon films.

reduced through the heat diffusion to the chamber wall and the sample. Hot gas molecules contact the chamber wall and the sample surface and heat them.

Figure 4 shows the changes in temperature of the Cr wires as a function of time for different initial total gas pressures between 220 and 500 Torr and the initial substrate temperature at room temperature. The temperature was calibrated from a relation between the resistivity of the Cr films and the temperature which was carefully measured using a furnace before the gas combustion experiments. The sample was rapidly heated during the initial stage. In the case of the initial gas pressure of 500 Torr, the temperature reached the maximum of 500°C within 2 ms. After reaching the peak, the temperature gradually decreased according to the rate of heat diffusion into the substrate. The full heating time at the half maximum temperature was 4.5 milliseconds for the initial gas pressure of 500 Torr, while it was 7.5 ms for that of 220 Torr. Figure 5 shows the maximum temperature heated by gas combustion as a function of the total gas pressure for the initial substrate temperatures at room temperature and at 300°C. The maximum temperature increased as the initial total gas pressure increased for both substrate temperatures. For the substrate temperature of 300°C, the temperature reached 800°C with the total gas pressure of 500 Torr. The same heating characteristics were obtained in the two Cr temperature sensors (see Fig. 1) within the measurement accuracy ($\Delta T \sim 12$°C). Figure 5 also shows the velocity of the combustion propagation, which was obtained from the retardation of the temperature change between the two Cr wires with 25 mm intervals.The propagation velocity of the gas combustion increased to 120 m/s at the sample surface as the initial gas pressure increased to 500 Torr. The propagation velocity in the middle region of the chamber was roughly estimated ~500 m/s at least for the 500 Torr-initial gas pressure case from the time difference between the combustion initiation given with a current change of W filament and the initiation of photo emission detection. The combustion propagates faster with the higher gas pressure because the mean free path of gas molecules is shorter and the probability of collisions between them is larger with a higher pressure. Moreover, the gas pressure of the combustion front is high because of the high temperature. The difference of the gas pressure between the reacted region and the unreacted region is larger for a higher initial gas pressure, making the gas combustion propagate faster.

The present heating method was applied to the activation of the dopant species in a semiconductor. 0.5-percent-phosphorus-doped-hydrogenated-amorphous silicon (a-Si:H, P(0.5%)) films with a thickness of 10 nm were heated by gas combustion with initial substrate temperatures of room temperature and 300°C. The electrical conductivity was increased from 4×10^{-7} S/cm to 7×10^{-4} S/cm as the initial total gas pressure increased to 500 Torr, as shown in Fig. 6. Some dopant atoms were activated during the combustion. Figure 6 shows the result that the present heating treatment has the possibility for rapid surface modification of semiconductor materials.

In summary, the gas combustion of H_2 with N_2O was investigated for use as a rapid thermal treatment. Cr films 100-nm-thick were used to measure the temperature at the surface of a quartz substrate. Spectra of the light emission caused by the combustion was analyzed based on the gray body irradiation theory. The gas temperature of 2200 K was achieved with an initial total gas pressure of 500 Torr ($[H_2]/[N_2O] = 1$). The gas combustion induced by a heated W filament propagated throughout the chamber. The propagation velocity is about 120 m/s at the sample surface for the initial total gas pressure of 500 Torr and it is estimated to be

$\sim$500 m/s in the center of the chamber. The sample surface was rapidly heated and reached a maximum temperature within 2 ms. The full time width at half maximum temperature was 4.5 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 heat to 800°C. The increment in the electrical conductivity was observed from 4×10^{-7} S/cm to 7×10^{-4} S/cm by the combustion for the 0.5%-phosphorus-doped-amorphous-silicon films. These results show that this method has possibility for use as a millisecond-order rapid thermal treatment.

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1) E. Landi, A. Armigliato, S. Solmi, R. Koegler and Wiser: Appl. Phys. A **47** (1988) 359.
2) T. Aoyama, K. Suzuki, H. Tashiro, Y. Toda, T. Yamazaki, K. Takasaki and T. Ito: J. Appl. Phys. **77** (1995) 417.
3) A. Kohno, T. Sameshima, N. Sano, M. Sekiya and M. Hara: IEEE Trans. Electron Devices **42** (1995) 251.
4) T. Young, G. A. Leeden, J. Narayan, W. H. Christe, R. F. Wood, D. E. Rothe and J. I. Levatter: IEEE Electron Device Lett. **3** (1982) 280.
5) P. G. Carey, K. Bezjian, T. W. Sigmon, P. Gildea and T. J. Magee: IEEE Electron Device Lett. **7** (1986) 440.
6) T. Sameshima, Y. Sunaga, N. Takashima and A. Tajima: Appl. Phys. Lett. **69** (1996) 1205.
7) A. Tajima, N. Takashima, Y. Sunaga and T. Sameshima: Proc. 1996 Solid State Devices and Materials, Yokohama, 1996, p. 245.
8) T. Sameshima, M. Hara and S. Usui: Jpn. J. Appl. Phys. **28** (1989) 12.
9) C. D. Hogman, R. C. West and S. M. Selby: *Handbook of Chemistry and Physics* (Chemical Rubber Publishing, Cleveland, 1959) p. 1802.
10) *JSME Combustion Handbook*, ed. The Japan Society of Mechanical Engineers (Maruzen, Tokyo, 1995) p. 119 [in Japanese].
11) G.W.C.Kaye and T.H.Laby: *Tables of Physical and Chemical Constants* (Longman, New York, 1973) 14th ed., p. 54.