LASER-IGNITED EXPLOSIVE DECOMPOSITION OF ORGANOMETALLIC COMPOUNDS

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A new type of laser-induced decomposition reaction of organometallic compounds and production of fine metal particles have been discovered in which a single laser pulse is used only for ignition of a thermal chain reaction. The formation of high density active species and the propagation of the reaction are discussed.

1. Introduction

Recently chemical vapor deposition has attracted much attention for the preparation of thin films and fine particles. In this process, laser beams are used for the decomposition of starting gaseous materials. However, a laser photon is effective on the average only to produce one or less product molecule and the quantum efficiency is usually low.

We have found a new process with an extremely high efficiency for producing fine metal particles from organometallic compounds, in which laser light is used only for igniting a decomposition reaction. The quantum efficiency exceeds 2×10^5. Chain reactions initiated by a CO_2 laser have been reported for the reaction of chromyl chloride with hydrogen to produce chromium oxide, water, and hydrogen chloride [1] and a reaction of vanadium oxychloride with hydrogen and oxygen to produce vanadium oxides [2]. In this Letter we report some features of a unique decomposition reaction of organometallic compounds.

2. Experimental

An excimer laser (ArF (193 nm) or KrF (248 nm)), having a fluence of 5–90 mJ/cm^2 and a pulse width of $\approx$10 ns, was used to decompose organometallic compounds. In some cases, with the KrF excimer laser irradiation, the laser beam was focused with a convex lens of 10 cm focal length in order to make active organometallic compounds at high concentrations. CO_2 and YAG lasers were also used for the investigation of laser wavelength dependence.

Tetramethyllead (TML), tetraethyllead (TEL), and trimethylbismuth (TMBi) were purchased from TRI Chemical Laboratory Inc. and their stated purities were 99.9999% based on metal analysis. These organometallic compounds were purified by at least five freeze–pump–thaw cycles followed by trap-to-trap distillation in vacuum before transferring them to the reaction cell.

Organometallic compounds were introduced into the reaction cell of about 100 ml volume. A reaction cell with a volume of 10 ℓ was used for the quantum efficiency measurement. Background pressure of 10^{-5} Torr was achieved by using an oil diffusion pump. All the experiments were carried out at room temperature. The shape and the size of metal particles were measured by a scanning electron microscope (Hitachi, S-800).

3. Results and discussion

3.1. Description of the explosive reaction

After organometallic compounds were introduced into the reaction cell, the sample was irradiated by

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a single laser pulse through a quartz window. Immediately after laser irradiation, most of the organometallic compounds decompose within a few tens of milliseconds accompanied by a strong orange emission from the whole volume of the sample cell. After that, fine black spherical metal particles having a size below 1 μm were deposited on the wall of the reaction cell.

There are two key points which make this unique reaction possible. One is the formation of high density active species by a single laser pulse irradiation and the second is the propagation of the thermal chain reaction.

High density active species such as metal atoms and methylmetal radicals are formed in a relatively confined volume because TML, for example, has a large molar extinction coefficient. These active species can cause the propagation of a thermal chain reaction. After the explosive reaction, most of the TML compound is decomposed to produce fine metal particles and ethane as the gaseous main product. Ethylene, methane, and propane are also observed as minor products by gas chromatographic analysis.

Now let us consider the efficiency of the reaction. The irradiated laser light, for example ArF 193 nm, 25 mJ, contains 2.4×10^{16} photons per pulse. On the other hand, 20 Torr of TML in a 10 ℓ volume reaction cell at room temperature (22°C) corresponds to 6.5×10^{21} molecules. Since more than 80% of TML is decomposed, the reaction quantum efficiency becomes at least 2.2×10^{5} which is limited by the volume of the container.

3.2. Laser fluence and laser wavelength

Fig. 1 shows the laser fluence dependence and laser wavelength dependence for the explosive reaction. In this figure, the vertical axis is the ratio of pressure after laser irradiation to that before irradiation. If the decomposition reaction of TML proceeds completely according to the scheme

$$(CH_3)_4Pb \rightarrow Pb + 2C_2H_6\,, \qquad (1)$$

this ratio should be 2, because the main gaseous products are 2 molecules of ethane from the recombination reaction of methyl radicals. In fact, most of TML in the reaction cell is decomposed and 85% of ethane, small amounts of methane, ethylene, and propane are detected by gas chromatograph.

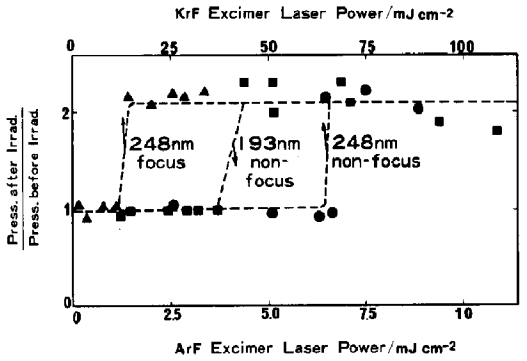

Fig. 1. Laser power dependence and laser wavelength dependence for the explosive chain reaction. Plotted on the vertical axis is the ratio of the sample pressure after and before laser irradiation. A value of about 2 indicates the occurrence of the chain reaction and unity the absence of the chain reaction (see text). The horizontal axis indicates the ArF excimer laser fluence (indicated below) and KrF excimer laser fluence (indicated above). The KrF excimer laser was focused with a convex lens (focal length = 10 cm).

As is clearly shown in this figure, for 5 Torr of TML, there exists a threshold laser fluence, about 5 mJ cm^{-2} in the case of 193 nm irradiation and 60 mJ cm^{-2} in the case of 248 nm irradiation. When the KrF excimer laser beam is focused with a convex lens, having 10 cm focal length, at a distance of 80 mm from the window, the threshold laser fluence goes down to 10 mJ cm^{-2} at 248 nm irradiation. These results indicate that a multiphoton process is probably necessary for the formation of active species.

The difference in the threshold laser fluence between 193 and 248 nm irradiation can be interpreted by the difference in absorption coefficients of TML at these wavelengths. The molar extinction coefficient is 1.03×10^{4} M^{-1} cm^{-1} at 193 nm, while it is 120 M^{-1} cm^{-1} at 248 nm. Accordingly the one-photon absorbance at 193 nm is about two orders of magnitude greater than at 248 nm. We have investigated the explosive reaction with other high power lasers, CO_2 and YAG, and observed it by focusing the laser beams. These results on laser power and wavelength dependence clearly show that it is very important for this reaction to produce high density active species.

3.3. Organometallic compounds possible to induce chain reaction

Among the organometallic compounds we have investigated at the present stage, TML and TMBi decomposed explosively. These two compounds have low metal–carbon bond dissociation energies. As the bond dissociation energy decreases, organometallic compounds can be expected to decompose to smaller fragments such as methylmetal radicals and metal atoms. Previously we have detected absorption spectra of the lead atom by the nanosecond laser flash photolysis technique [3]. In the case of the photolysis of hexamethyldisilane, only trimethylsilyl radical can be detected [4]. Accordingly active species are expected to be generated in the photolysis of compounds with a weak bond dissociation energy. These compounds are also advantageous for the propagation of thermal chain reactions.

Among the various types of organometallic compounds, alkylmetal, metalcarbonyl, metal halogen, and metallocene compounds have weak bond dissociation energies. Decomposition of some of the alkylmetal compounds can be exothermic because the recombination of alkyl–alkyl radical is highly exothermic. Table 1 shows the average bond dissociation energy (D_n) and energy balance (ΔH) of some alkylmetal compounds. ΔH is calculated by the bond dissociation energy of the alkylmetal (D_n) minus bond formation energy of the alkyl–alkyl radical, for instance, the bonding energy of methyl–methyl is 368 kJ mol^{-1}. The compound which has a negative ΔH value, that is, the one proceeds an exothermic reaction, has a possibility of producing a chain reaction. In fact, TML and TMBi can cause a chain reaction. On the other hands, some compounds, which have negative ΔH, did not cause a chain reaction. This is presumably because of the low vapor pressure at room temperature and for other unknown reasons.

Table 1
Bond dissociation energy (D_n) and ΔH of reaction, $MR_4 \rightarrow M + 2R-R$, for some alkylmetal compounds (in kJ mol^{-1})

Alkylmetal compound	D_n	ΔH
$Bi(CH_3)_3$	428	−124
$Pb(CH_3)_4$	632	−104
$Pb(C_2H_5)_4$	512	−224
$Sn(CH_3)_4$	896	160
$Ge(CH_3)_4$	1040	304
$Si(CH_3)_4$	1276	540
$Zn(CH_3)_2$	351	−17
$Zn(C_2H_5)_2$	290	−78
$Cd(CH_3)_2$	279	−88

3.4. Effect of concentration of organometallic compounds

The reaction does not take place below a concentration of ≈1 Torr in both cases of 193 and 248 nm irradiation. This pressure effect can be interpreted as follows. When the pressure of the starting materials is low, active species which are formed by the laser irradiation, cannot collide with the other parent molecule and will perhaps be deactivated by a collision with the wall. On the other hand, with higher pressures, active species can collide with an other parent molecule and transfer the internal energies to it. The frequency of collision is attributed to the pressure of the parent molecule. The excited parent molecule then decomposes to form active species again and thermal chain propagation proceeds. Fine metal particles and gaseous products are formed during the propagation of the chain reaction.

3.5. Effect of foreign gases

The effect of foreign gases for the explosive reactions is shown in fig. 2. Under this condition, the chain reaction is prohibited by the addition of for-

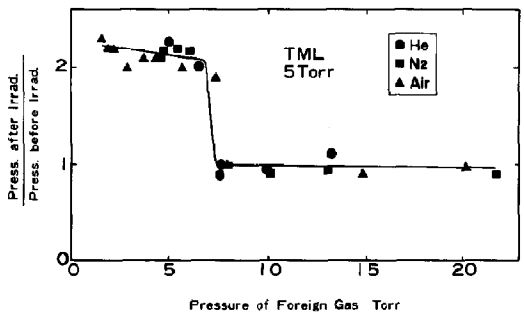

Fig. 2. Effect of foreign gases. Plotted on the horizontal axis is the pressure of foreign gases added to 5 Torr of tetramethyllead (TML) under the same reaction conditions. Vertical axis is the same as fig. 1.

eign gases (He, N_2, air) above 7 Torr at the pressure of the parent molecule (TML) of 5 Torr. This result can be interpreted as the deactivation of active species by added foreign gases. When concentration of foreign gases is low, the active species can collide with the other parent molecules. However, upon increasing the foreign gas pressure, a possibility of the collision with foreign gases increases, and finally the active species cannot propagate the thermal chain reaction.

In conclusion, we have discovered a unique laser-induced decomposition reaction of organometallic compounds. Since this reaction is initiated by only a single shot of laser irradiation and causes an explosive reaction, we would like to call this type of decomposition reaction as "laser-ignited mild explosive reaction (LIMER)". The key points of LIMER are the high density formation of active species and the propagation of thermal chain reaction caused by these active species. The reaction mechanism and the properties of emission are now under investigation. The details of these results will be reported in the near future.

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