

Design of LICVD equipment for preparation of nano powder and study on laser threshold

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A laser-induced chemical vapor deposition (LICVD) nanometer equipment is designed and fabricated. The design conception of key parts is expatiated. The energy threshold of SiH_4 decomposing is studied. In the condition of same reactive gas flux, the laser energy threshold decreases with the increase of SiH_4 concentration. In the condition of same SiH_4 concentration, with the increase of reactive gas flux, the laser energy threshold which induces SiH_4 decomposition increases linearly at the beginning, and when the flux is more than 100 ml/min, it turns to increase slowly. The factors which influence the laser threshold are analyzed.

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Since the successful preparation of Fe-based nano-grain by Gleiter in 1984^[4], the preparations, properties, and applications of nano-materials, especially the preparations have been studied extensively. The preparation technology in studying Si-based nano-material is also very important, which has been widely improved in recent years. The crystalline condition of product, appearance, and grain size are influenced directly by the preparation technology. In addition, the physical and the chemical functions of the nano-materials are decided finally by the preparation technology.

The principle of the laser-induced chemical vapor deposition (LICVD) equipment is that the reactive gas SiH_4 absorbs the special wavelength laser ($10.6 \mu\text{m}$), being heated and dissociated into saturate Si steam, then the steam will become cores and grow up for the nanometer silicon particle during the course of transporting.

The LICVD facility was equipped with a reactive chamber, a continuous wave (CW) CO_2 laser, an air feed system, a collector, a vacuum system, and a cooling system. We used the reactive chamber for chemical reaction, and forming cores, which are the key of the LICVD facility. The structure and the design of the inner components are crucial to the nano-grain appearance, physics, and the whole experiment.

The reactive chamber was made up of stainless steel. The reactive gas entered the reactive chamber from the portal. The CO_2 laser beam passing by the ZnAs incident window, focused near the axis of the reactive chamber. The jet direction of the reactive gas was perpendicular with the laser beam. High purity argon gas was blew around the reactive gas and the inner face of incident window, while the created nano-powder was led to the powder collector by the argon gas (see Fig. 1). The facility photograph of LICVD is shown in Fig. 2.

The optical system included the laser entrance window and the absorbing window. The function of the laser entrance window was to focus the parallel CO_2 laser beam by the ZnAs convex lens, so that the energy can irradiate on the reactive gas with a smaller spot.

In order to avoid the damage of ZnAs focusing lens caused by the increase of temperature, the sealing cover should be made by pure copper, a material with good thermal conductivity, and be cooled by

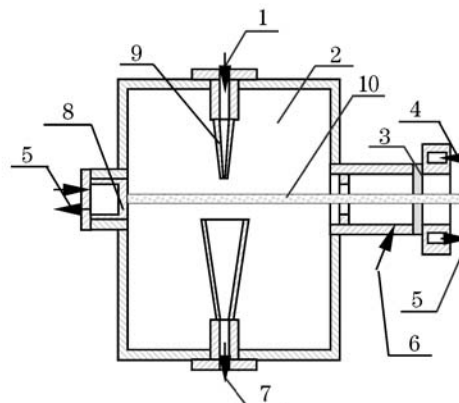


Fig. 1. The facility sketch of LICVD. 1: portal of reactive gas; 2: reactive chamber; 3: incident window; 4: portal of cooling water; 5: export of cooling water; 6: portal of Ar; 7: powder collector; 8: laser absorb seat; 9: gas nozzle; 10: laser beam.



Fig. 2. The facility photograph.

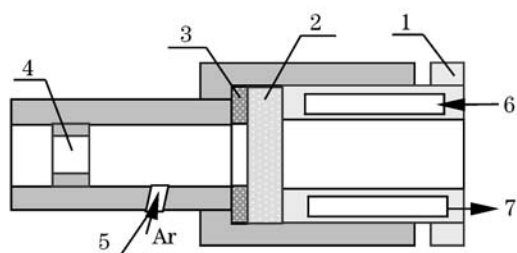


Fig. 3. The system of the light window. 1: water-cooling cover; 2: ZnAs focusing lens; 3: O-type sealing loop; 4: dirt-preventing ring; 5: portal of protection gas; 6: portal of cooling water; 7: export of cooling water.

flowing water (see Fig. 3). A portal of protection gas was designed after the lens, preventing the ZnAs focusing lens from the nano-powder pollution. We made the entrance of the gas sloping to the lens, which protects the focusing lens from high temperature. Meanwhile, for more efficiently protecting the focusing lens, a dirt-preventing ring was inserted between the light window and the reactive chamber. The dimension of the dirt-preventing ring should be decreased as possible. It can not only reduce the effective area through which the nano-powder enters the light seat, but also decrease the flux of the protecting gas and protect the lens from being polluted by the nano powder.

During the preparation of nano-powder by the LICVD equipment, only a fraction of the laser energy was absorbed by the reactive gas. So we must design a laser absorbing seat facing to the incident window for absorbing the surplus laser energy. The laser absorbing seat was made by pure copper, and was water-cooled in the middle by force. We shaped it into concave and treated its surface by sand blast to prevent other destroys by the reflection of the laser beam. To increase its absorption coefficient, we covered the surface of the laser seat with a layer of carbon.

The reactive chamber was also equipped with a vacuum gauge, a barometer, and an observing window. We used the vacuum gauge to measure the vacuum degree during the preparation of the powder, and the barometer to monitor the pressure in the chamber. The observing window was used to observe the shape of flame and measure the temperature of the flame by infrared radiation thermometer.

In the LICVD equipment, the flow of the gas in the reactive chamber directly influenced the crystal nucleation and growth of the nano-powder. If the pressure in the reactive chamber was low, the reaction gas would expand by the sudden drop of the surrounding pressure when the reactive gas passed through the nozzle. In addition, the absorbing of the laser energy would also lead the gas to expand rapidly. Thus the diameter of the reactive gas stream will become wide immediately after passing through the portal. If the diameter of the interface of the laser beam and the reactive gas was larger than that of the laser spot, the gas will not be completely resolved. Therefore, we adopted the following measures in the design of the spray nozzle (see Fig. 4). 1) Considering to produce an axial component force to offset the expanding force, we designed the spray nozzle into cone-shape. 2) Protecting the reactive gas with a "shell" of argon gas.

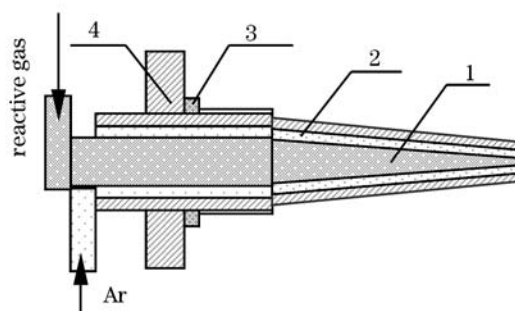


Fig. 4. The spray nozzle. 1: portal of reactive gas; 2: portal of coaxial gas; 3: O-type sealing loop; 4: tract of nozzle.

On the one hand, the argon gas would produce an axial pressure to keep the reactive gas from inflating. On the other hand, it can limit the reactive field to increase the collision probability of the reactive product and improve the nucleation rate.

Meanwhile, for preventing the reactive gas from extending, we made the laser beam and the reactive gas intersecting at the front of the convergent point, which would diminish the divergence of the reactive flame because there was an axial component force for the reactive gas.

The function of the collector was to separate the produced powder from tail gas and collect the powder. Because the nano powder made by LICVD equipment was small (generally tens of nanometers) and light, it was easier to suspend in the reactive chamber to affect the reaction. Consequently, the produced nano-grain must be collected and discharged timely and rapidly. For this reason, we designed the collector into cone-shape and decreased its distance to the spray nozzle, which can obviously improve the collecting efficiency. The tail gas and the nano-particle were led into a filter bag which was made up of several layers of cloth and contained an air-washing bottle. Then most of the nano-powder was in the filter bag. There was a piece of defatted cotton, which filtered the tail gas for the second time, at the outlet of the air-washing bottle. After this the tail gas was discharged through the vacuum pump.

In order to control the exhausting speed of the vacuum pump and keep the pressure of the reactive chamber constant, we installed a gas flux control valve between the air-washing bottle and the vacuum pump. By adjusting the valve, we can control the gas pressure in the reactive chamber conveniently to meet different demands of technological parameter of preparation.

The principle of LICVD method is to utilize the strong absorption characteristic to specific wavelength laser beam of the reactive gas (or photosensitive pharmaceutical molecule). This characteristic would cause laser resolving, laser heat-solving, laser sensitization, and laser-guided chemical reaction. Compared with other lasers, CO₂ laser has the following advantages: the high electrical-to-optical conversion efficiency, the high output power, the steady and good performance. Especially, the 10.6- μm main line happens to be in the range of "atmospheric window", that is, the transmittance of laser at this wavelength in air is very high. The laser beam can propagate a very long distance in the air environment and the power loss is very little. In this experiment sys-

tem, we adopted CW CO₂ laser instrument as the heat source, the power was continuously tunable in the range of 100–2000 W.

The even and stable air supply system was essential for preparing uniform nano-particles. During the preparation, any fluctuation of air supply would influence the size and shape of the produced particles. For avoiding the fluctuation, we made each air supply system with an independent air supply cylinder and an independent compression release valve.

The viscosity of SiH₄ gas was strong. For ensuring the gas be diluted evenly, we set up a special gas mixing room. Each branch of the air supply system was equipped with a flow meter and a needle-like regulate valve, which precisely controlled the content of different kinds of gas.

The cooling water system and the vacuum system were attached to the LICVD nanometer equipment. The main action of the water was to cool down the laser entrance window and the laser absorbing seat, avoiding the burst of lens and metallic vapour. The main function of the vacuum system was to deliver the tail gas with the produced nano powder from the reactive chamber to the collector and exhaust the waste gas. Moreover, it ensured that the reaction carried out under the certain air pressure. The experimental parameters are shown in Table 1.

In this study, the SiH₄ gas was diluted by the high purity argon, and the purity of SiH₄ gas is 99.9999%. The components of reactive gas used in 8 different experiments are 5%, 10%, 15%, 20%, 25%, 30%, 35%, and 40%.

While using LICVD method to prepare silicon nanometer material, the laser was made to act as a heat source to resolve the gas and then from cores. So the power density of laser influenced the characteristics of the powder greatly. In order to investigate the impact of the power density of laser on silicon nanometer powder characteristics, we adopted CW CO₂ laser (SPECTRA820) as heat-solving light source, the power of laser was continuously tunable from 100 to 1500 W. The values of flux

Table 1. The Experimental Parameters

Parameter	Value
Nozzle Diameter of Reactive Gas (Inside/Outside) (mm)	2/4
Diameter of Co-Axial Nozzle (Inside/Outside) (mm)	8/12
Lens Focal Length (mm)	220
Distance between Nozzle and ZnAs Lens (mm)	200
Distance between Focus Spot and Nozzle (mm)	2
Pre-Vacuum of Reactive System (Pa)	1
Diameter of Focus Spot (mm)	6

Table 2. The Flux of Gases Used in the Experiment (Unit: ml/min)

Gas	Reactive Gas	Co-Axial Gas	Glass Protecting Gas
Flux	20	240	1000

of the gases were listed in Table 2.

The reactive chamber was opened at first, and then the laser system was turned on. While putting the warrior paper on the spray nozzle, we adjusted the laser to make the spray nozzle receive a round spot with a diameter of 6 mm. After the reactive chamber was sealed, the vacuum system was opened till the pressure released under 1 Pa. Next, the argon gas valve was opened for 5 minutes in order to further empty the impurity gas. Lastly, the values of flux of the ring-type gas and the protective gas of laser entrance window were regulated to 240 and 1000 ml/min, respectively, at the same time the needle valve on the air-bleed pipe was regulated to enable the pressure steady at 80 kPa.

The laser system was started with the lowest output power, and the reactive gas valve was opened. We adjusted the proportion of SiH₄/(SiH₄+Ar) to 5%, the reactive gas flux is 20 ml/min.

Increasing the output power of the laser slowly, we observed whether there was brown gas emerging in the collector. At the same time, we observed the reactive flame in the intersection of the reactive gas and the laser spot. Stop regulating the power of laser immediately when we found brown gas emerging in the collector. The power of laser at this moment was the critical value of the reactive gas under this condition, which was the threshold value. Repeating the above-mentioned process, we adopted the components of the reactive gas as Table 2 and recorded the threshold values respectively. The

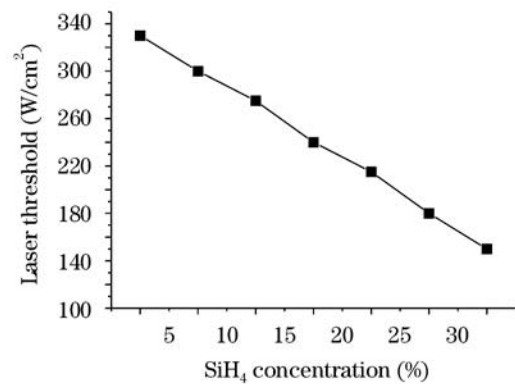


Fig. 5. The relation between SiH₄ concentration and laser threshold.

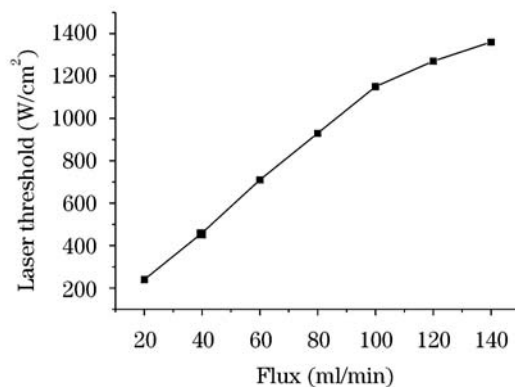


Fig. 6. The relation between reactive gas flux and laser threshold.

experimental results are shown in Fig. 5.

The concentration of SiH_4 gas was fixed at 20%, and the flow velocities of the glass protecting gas and the co-axial gas were kept unchanged. The flux of reactive gas was set to be 20, 40, 60, 80, 100, 120, 140, and 160 ml/min for the other 8 different experiments. Under the same conditions as before, we investigated the relation between the reactive gas flux and laser threshold. The experimental results are shown in Fig. 6.

From Fig. 5 we can find that the laser threshold is reduced with increasing the concentration of SiH_4 . In this reactive system, only SiH_4 can strongly absorb the CO_2 laser, so it can be resolved when the reactive gas goes through the laser spot. When the gas flows, SiH_4 gas transmits some energy to argon gas by the mutual collision. With low SiH_4 concentration, most of the laser energy absorbed by SiH_4 is transmitted to the surrounding argon gas, so it needs to absorb more energy to resolve and the laser threshold is relatively high. On the other hand, because the energy for heating argon gas is low, the laser threshold is relatively low with higher SiH_4 concentration. Meanwhile, we draw the conclusion that there is a linear relationship between the laser threshold and the SiH_4 concentration under the constant gas flux.

From Fig. 6, if the concentration of SiH_4 keeps constant, the laser energy for resolving SiH_4 increases linearly at first, but when the gas flux exceeds 100 ml/min, the laser threshold increases slowly. We think that under the low gas flux (<100 ml/min), the flow increases in step with the increase of the velocity of gas flux, the

reactive gas spends less time to pass through the laser area, thus we must raise the power density of laser in order to improve the absorption coefficient of the reactive gas. Under the high flux of gas (>100 ml/min), the co-axial argon gas cannot suppress the reactive flame, which leads to radial dilation of the reaction gas and increases the effective absorption of laser energy, the threshold increases slowly.

In conclusion, we designed and made the preparation equipment of nano powder by LICVD. The laser energy thresholds under different conditions were studied. Under the constant flux of the reactive gas, the threshold is reduced with increasing the concentration of SiH_4 , there is a roughly linear relationship between them. With the concentration of SiH_4 gas fixed, and changing the flux of reactive gas, the threshold for resolving SiH_4 increases linearly at first, but when the gas flux exceeds 100 ml/min, the threshold increased slowly.

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