Study of the Plasma Chemistry of sealed-off CO_2 Lasers with Novel Mass-spectrometric Technique Part I. Experimental Technique.

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ABSTRACT

A novel mass-spectrometric technique for lifetime studies of sealed-off CO_2 gas lasers as well as other plasma devices is presented.Factors influencing accuracy are discussed and methods for overcoming them are introduced.

A CO_2 gas laser, either the CW type or the TEA type, when turned on, considerable plasma chemical processes proceed, which lead to degeneration of the laser mixture, mainly, the decrease of CO_2 concentration. When a stage at which the CO_2 concentration becomes too low arrives, the laser tube fails to work, i.e., its lifetime is end. The same problem also takes place in other discharge devices of limit volume, for example, the discharge lamps.

To investigate the lifetime of such devices, the effective method is to analyse the variation of gas components. But up to now, accurate mass-spectrometric technique is still lacking for such sealed-off devices. In recent years, novel mass-spectrometric technique suitable for this purpose has been developed in our laboratory, and meaningful results have been achieved[1~3].In this paper, the author will present this technique which includes five contents, as follows.

1. Making an ultramini-flow valve The main diffi-

culty arising in gas analysis of sealed-off devices is the depletion of gas amount which,in turn,changes the device characteristics. Generally, to ensure the mass-spectrometer tube from oxidation,differential pumping method in which continuous pumping through a high impedance is provided is used. The high impedance was a leak or a long capillary tube[4]. These methods possess a characteristic of narrow channel/long tube flowing,appearing a mass-discriminative effect which introdcues considerable error to the results. Besides,for the case of gas leak,the impedance is unstable due to obstruction of dirty materials; thus they cannot be safely used for long-term experiments,i.e.,lifetime studies. To overcome these disadvantages, a new designed valve, the so called "ultramini-flow valve" has been made,as shown schematically in Fig.1. It is,to some extent, like a traditional diaphragm valve,consisting of a glass plate,which has an extremely small hole at the geometrical centre, and is stuck to the valve envelope at an appropriate position, a Viton membrane, with a rubber disc at its top just front of the hole,and an operational mechanism to move the membrance back and forth. When the rubber disc is pressed on the glass plate, the hole is shut off and the valve is closed, when it is left, the valve is open. This valve only has two states: the closed state and the open state. It does not have the partially open state of a needle valve;when opened, the flow rate is independent of temperature,as the expansion coefficient of the glass plate is small. The hole was thin enough that the gas flow can be regarded as a molecular flow through a hole, thus its mass-discriminative effect is negligible.

2. heightenning the pressure-range of the valve Long period application showed that this type of valve with single hole was merely suitable for analysis of gases with pressure lower than 10 KPa. If the pressure is higher than this value,it fails to preserve the pressure-linearity. so

an improvement for it was necessary.The basic concept is as follows. To fit the requirement of pressure-linearity, the gas flow,(when the valve is opened) must be in the molecular flow regime, i.e. consider the Knudsen number $d/\lambda > 1$, where d is the diameter of the hole, and λ is the mean free path of the gas molecules[5]. The hole diameter was approximately 10 μm in the single hole valve, thus its pressure-linearity was merely up to several hundred Pa.If we want to raise the linearity up to at least one atmosphere, a rough estimation showed that the hole-diameter must be less than 0.06μm. Such a hole has too small a conductance, so that it could not provide enough partial pressure for the quadrupole tube. To overcome this difficulty,a realistic method is to use a huge number(n) of parallel holes with diameters near 0.06μm. By adjusting the number n,one can obtain a suitable "hole-array" with appropriate conductance,and based on this, a high pressure ultramini-flow valve can be made, working in the molecular flow regime. To make such a valve, several porous materials such as ceramics, and porous nickels,have been tested, and finally, an appropriate kind of porous nickel(the so called B-type nickel) with an average hole diameter of 0.07μm was chosen. Replacing the single-hole-glass plate by a porous nickel piece, we have a new valve having pressure-linearity up to 133 KPa.

3. Overcoming the sensitivity-fluctuation of the mass-spectrometer. The mass-spectrometer used was a quadrupole one. As well known, its sensitivity often varies due the formation of insulating film by polymerization of silicone oil vapor or other organic vapor.The insulating film changes the electric field distribution,leading to a decay of the sensitivity[6,7]. To eliminate this variation thoroughly, at present time,seems impossible. Thus a comparing method was applied to revise the readings. Practically, a sample gas bottle was also arranged in the set up. The bot-

tle and the laser tube were connected to the quadrupole tube with ultramini-flow valve of its own, and both were filled with the same laser mixture. When testing, the ultramini-flow valves were operated in succession to take spectrum of its own.As the room temperature was kept constant(15°C), and the bottle was large enough to keep gas quantity constant, the spectrum of the sample gas should be repeatable; thus any fluctuation of it can be considered as causing by the sensitivity-variation of the spectrometer. This was used to revise the spectra of the laser tube.

4. Evaluating the time delay The ultramini-flow valve divides the set-up into two regions: the high vacuum region and the high pressure region; great pressure differences arose across the valves. For connecting,a glass pipe with a length of L and a dia. of D was used to connect the laser tube/sample bottle to the ultramini-flow valve. It is apperent that any change-information of gas components inside the laser tube/sample bottle will arrive at the valve by a delay time which depends on L,D and the pressure within it. Because the gas pressure is relatively high in this pipe, diffusion is considerably slow. Theoretical and experimental studies on this problem have been performed,the results showed that under general condition, the delay time is from several minites to several ten minites[8]. The delay time τ is defined as the time neccesary for the peak-height to arrive 63 % its final steady value, and this quantity was taken as a "waiting time" for beginning to record mass-spectrum.

5. Keeping the moisture of the envirenment constant We found that in the residual spectrum (background vacuum) the peak-height of 18 (H_2O) was seriously depending on the moisture of the room. This is because moisture can through the rotary pump by "riding" on the circulating oil,in turn, through the turbomolecular pump by back-diffusion. Thisproblem was solved effectively by using a 5 KW moisture coll-

lector.

In summary, the set-up developed in our lab is shown in Fig. 2; and the procedure for acheiving high accuracy and good repeatability is as follows. Firstly, outgas the whole vacuum system,including the quadrupole tube thoroughly, by electric heating strip; secondly,fill the laser tube as well as the sample gas bottle with laser mixture, and isolate them by sealing at point M,N; thirdly,turn on the electronic circuit of the mass-spectrometer for an hour to reach stabilization; finally,start taking readings. The moisture collector should be always turned on.

REFERENCES

1. Wang Y.Z.,Liu,J.S. J.Appl.Phys.59(1986),1834-1838
2. Wang Y.Z.,Yang,Z.M. J.Phys.E:Sci.Instrum. 20(1987) 1483-1486
3. Wang Y.Z. Optics & Laser Tech.25(1993)367-370
4. Hirsh M.N. & Oskam H.J. Gaseous Electronics, Vol.1. Academic Press (1978), 141-145
5. Roth A. Vacuum Technology, North-Holland (1976) 60-62
6. Mao F.M.,Austin,W.E. Vacuum 37(1987) 335-339
7. Austin W.E.,Moa F.M. J.Vac.Sci.Technol. A5(4) 2631-2637
8. Huang Z.L. Vac.Sci. & Tech.(China) 10(1990) 128-133

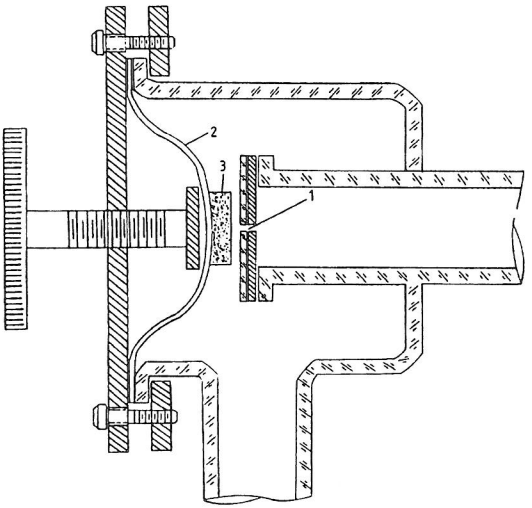

Figure 1. Ultramini-flow valve. 1, extremely small hole; 2, Viton membrane; 3, rubber disc.

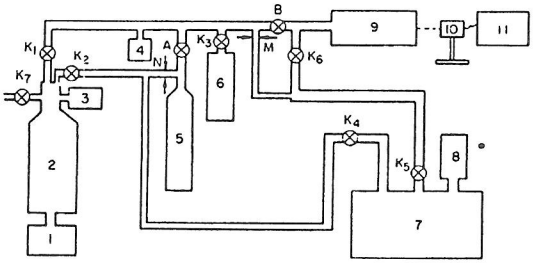

Figure 2. Experimental set-up. 1—mechanical pump; 2—turbomolecular pump; 3, 4—B-A gauges; 5—sample gas bottle; 6—quadrupole tube; 7—gas supply system; 8—HLP-03 vacuum gauge; 9—TEA CO_2 laser tube; 10—sensor; 11—laser energy meter, $K_1 \cdots K_6$—ultra-high vacuum valves; K_6—glass high vacuum valve; A, B—high pressure ultramini-flow valves