Microwave-induced plasma reactor based on a domestic microwave oven for bulk solid state chemistry

David J. Brooks and Richard E. Douthwaite[a)]
Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom

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A microwave-induced plasma (MIP) reactor has been constructed from a domestic microwave oven (DMO) and applied to the bulk synthesis of solid state compounds. Low pressure MIP can be initiated and maintained using a range of gases including Ar, N_2, NH_3, O_2, Cl_2, and H_2S. In order to obtain reproducible synthesis conditions the apparatus is designed to allow control of gas flow rate, gas composition, and pressure. The use of the reactor is demonstrated by the synthesis of three binary metal nitrides formed in a NH_3 MIP. The reactions are rapid and the products show good crystallinity and phase purity as judged by powder x-ray diffraction. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1821623]

I. INTRODUCTION

The application of microwave dielectric heating is now an established method for the rapid preparation of compounds in solution based synthetic chemistry.[1,2] Commercial laboratory instruments are now available providing excellent power and temperature control. In contrast, in the solid state, the use of microwave methods remains underdeveloped and there have been relatively few reports describing the synthesis of bulk compounds using microwave techniques.[3]

The majority of bulk solid synthetic work utilizes dielectric or conduction loss heating of one or all of the solid precursors to drive the chemical reaction.[3] However many solids do not exhibit dielectric or conduction loss at room temperature therefore limiting the application of microwave heating. To circumvent this problem a microwave susceptor can be added that mediates energy transfer between the microwave electric field and solid precursors. However disadvantages of using a susceptor are that it may require removal, or participate in unwanted side reactions. For example, amorphous carbon is a commonly used susceptor, but carbon is also a powerful reducing agent.[3–6]

Microwave-induced plasmas (MIPs) are used extensively for surface modification[7] and the vapor deposition of thin films[8,9] but have been rarely used for bulk synthesis. The main advantage of MIP for solid state chemistry over dielectric and conduction loss heating is that any solid immersed in the MIP will heat. Another feature is that the plasma may also serve as a source of reactive species for bulk solid state modification.

There are a limited number of reports describing MIP bulk synthesis and all but one,[10] use commercial single mode microwave cavities that are expensive relative to the apparatus described herein.[11–15] MIP can be generated in glass tubes sealed under a partial pressure of gas, however, this method is limited for bulk synthesis because under the reaction conditions the plasma can quench due to pressure fluctuations and also by-products cannot easily be removed. A MIP flow reactor based on a DMO has previously been reported, however the authors stated that the apparatus was unable to reproducibly initiate and maintain a MIP (of N_2) and therefore opted for a commercial single mode cavity for their study.[15]

We describe the design, construction, and utilization of a simple low cost MIP flow reactor based on a DMO. The reactor can ignite and maintain plasmas of a wide range of gases and has been used for the MIP ammonolysis of some metal oxides to the corresponding nitrides.

II. INSTRUMENTATION

The microwave reactor is based on a Panasonic NNT551, 2.45 GHz, DMO, which is unusual among DMOs in that continuous application of microwaves is available at several power settings (900, 600, 440, 250, and 100 W). This is in contrast to most DMOs where a lower power setting is achieved by modulation of a single incident power to the magnetron. The main features of the apparatus are designed to achieve reproducible synthesis conditions and allow the manipulation of air sensitive precursors or products.

A schematic of the apparatus is shown in Fig. 1. A slot cut into the back of the cavity wall allows access for a silica U tube (internal diameter 20 mm) that contains the sample in an alumina boat. The U bend is connected via two Teflon stopcocks fitted with B24 Quickfit joints to the gas inlet system and a vacuum pump (Leybold Trivac D5 E rotary oil pump), respectively. A gas manifold constructed from Swagelock incorporates two Brooks 5850TR mass flow controllers and a Leybold Piezovac PV 20 pressure gauge to control gas flow rate, gas composition, and pressure.

To limit stray radiation and locate the U tube in the desired position a mounting plate is used that fixes onto the back of the cavity as shown in Fig. 1. To further limit stray radiation two porous steel baffles are also positioned in the U tube and a Faraday cage constructed from porous steel mesh encloses the gas inlet–outlet system.

[a)]Author to whom correspondence should be addressed; electronic mail: red4@york.ac.uk

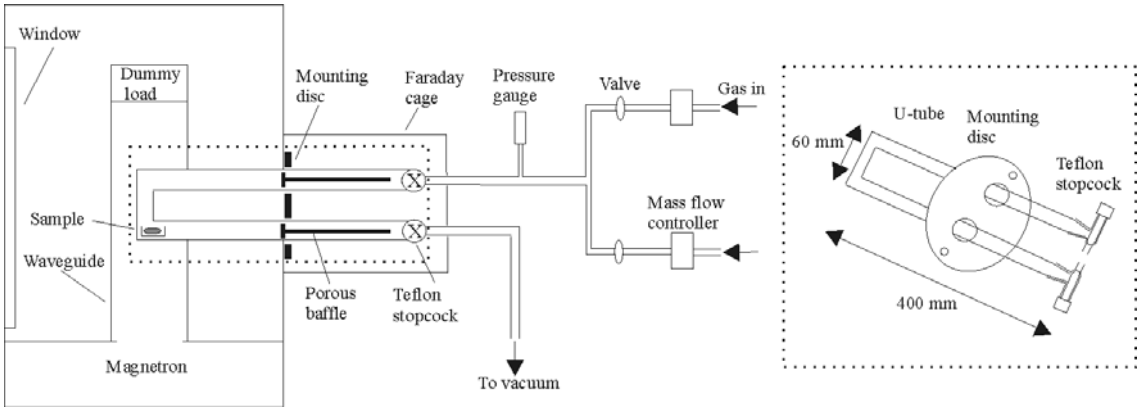

FIG. 1. Schematic of MIP reactor. The portion of the apparatus shown in the dotted box can be isolated to allow the manipulation of air sensitive products and precursors.

In order to manipulate air sensitive products and precursors the dimensions of the U tube, mounting disk, and Teflon stopcocks are collectively small enough to fit into the port of a drybox. In a typical loading procedure the sample is placed in the U tube on an alumina boat, the baffles are inserted and the Teflon stopcocks fitted to seal the U tube. The U tube is then connected to the vacuum outlet and the gas inlet system, which if necessary, is prepurged with a flow of argon.

In initial experiments it was found that plasmas derived from Ar, N_2, $5\%H_2/N_2$, NH_3, and O_2 between $\sim 1-50$ mbar could be initiated and maintained for an indefinite period of time. Except for argon all MIPs are confined within the volume in the cavity between the porous steel baffles. At pressures below 13 mbar, an Ar MIP extends ~ 100 mm beyond both the inlet and outlet baffles, but at higher pressures or on introduction of a second gas, the plasma remains in the cavity.

The equilibrium temperature experienced by samples immersed in the plasma was estimated by exposing salts of known melting point sealed in silica capillaries to a MIP for 10 min. Melting was taken to indicate that the equilibrium plasma temperature was equal to or exceeded the melting point of the salt. Within the limits of available standards it was found that the maximum temperature obtained was between 1043 (melting point of KCl) and 1074 K (NaCl) for all the gases at 900 W and surprisingly that there was no significant power or pressure dependence over the available ranges.

To increase the equilibrium temperature, a box section of brass (internal dimensions $310 \times 80 \times 35$ mm) was fixed to the microwave inlet to act as a waveguide, focusing the microwaves in the vicinity of the sample. An image of the interior of the reactor is shown in Fig. 2. A slot cut into the waveguide centered at 210 mm $(7/4\ \lambda)$ from the magnetron was used to locate the U bend in an area of large electrical field intensity. To prevent reflected power damaging the magnetron and the waveguide overheating, water is circulated through copper piping soldered to the waveguide and connected to a 500 mL dummy load vessel placed at the waveguide exit. Due to the dummy load very little power is reflected back into the waveguide and the apparatus could now be considered to be working in a single mode configuration, in contrast to the multimode configuration without the waveguide. The dummy load also reduces the possibility of arcing between the waveguide, cooling pipes or metal interior of the microwave cavity by absorbing stray radiation. At no point have we observed arcing in our apparatus.

Using the waveguide the equilibrium temperature of the plasma is increased. Argon gave a maximum temperature between $1157(Na_2SO_4)-1248$ K (K_2CrO_4) and the other gases between $1248-1400$ K $(MgSO_4)$ at 900 W again with no apparent power or pressure dependence.

In a further modification the mass flow controllers can be replaced with inexpensive Aalborg, model T flowmeters. Although there is some loss of precision of gas flow rate and mixed gas composition these flow controllers have the advantage of greater tolerance to many corrosive gases. Using this modification we can initiate and maintain plasmas of Cl_2 and H_2S.

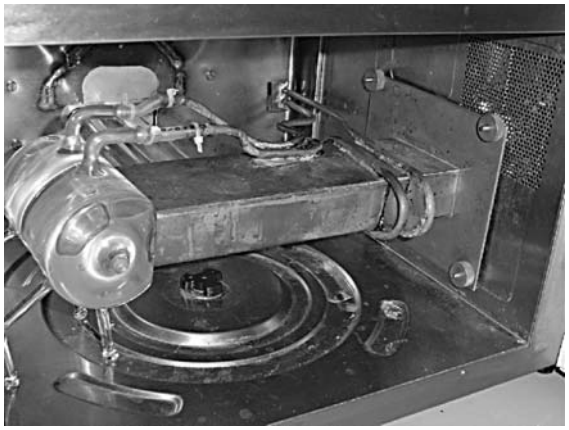

FIG. 2. Interior image of MIP reactor containing the waveguide and dummy load.

TABLE I. Results of MIP ammonolysis of metal oxides.

Precursor	Time (h)	Intermediate grindings	Product
Ga_2O_3	2.5	2	GaN
TiO_2	3.5	2	TiN
V_2O_5	6	3	VN

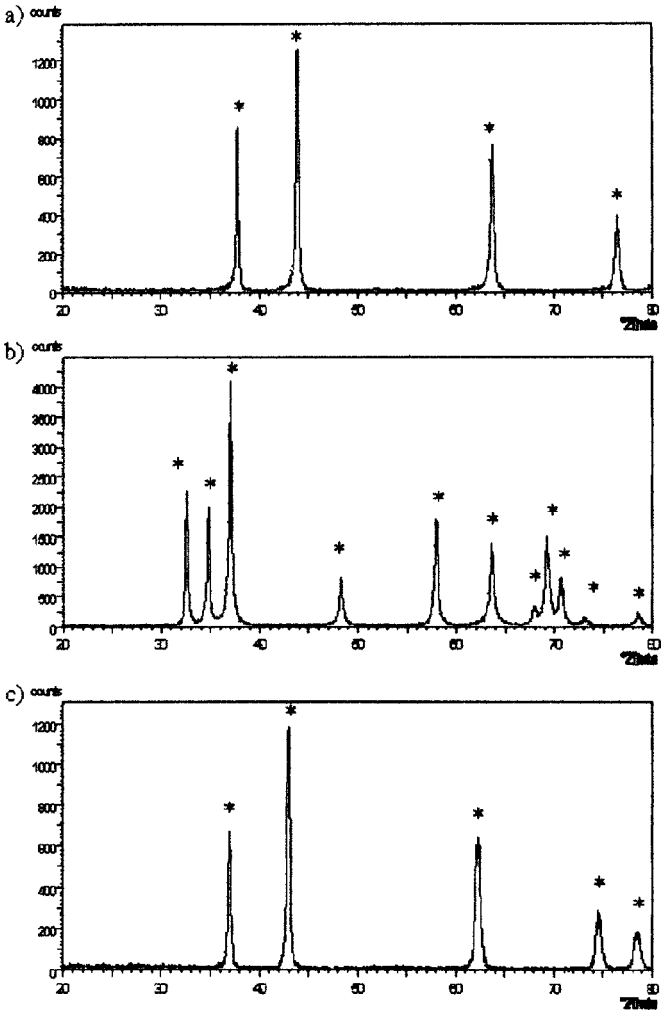

FIG. 3. Powder x-ray diffraction patterns of MIP synthesized binary metal nitrides. (*) reflections from JCPDS powder diffraction file (PDF): (a) VN (PDF-35-0768), (b) GaN (76-0703), (c) TiN (87-0632).

III. EXPERIMENTAL RESULTS

The use of our reactor was tested on the synthesis of a selection of binary metal nitrides using an ammonia MIP. It was found that without the waveguide the reactions were very slow and invariably did not go to completion and therefore all subsequent experiments were performed using the apparatus fitted with the waveguide.

In a typical experiment 2 g of a powdered metal oxide (Ga_2O_3, TiO_2, and V_2O_5) in an alumina boat is placed in the U tube and slowly evacuated to 10^{-2} mbar to avoid powder displacement. After evacuation ammonia was introduced at a flow rate of 113 $cm^3\,min^{-1}$ to give a convenient working pressure of 20 mbar. On irradiation at 900 W the plasma ignites within 3 s resulting in a bright purple glow. When plasma treatment is complete the sample is allowed to cool to room temperature over 10 min under flowing ammonia and subsequently the U tube is evacuated and filled with argon. The sample is then ground and analyzed by powder x-ray diffraction (Philips PW 1800) and peak position and intensity compared to values available from the JCPDS-International Centre for Diffraction Data.

The total duration of each experiment and number of intermediate grindings is shown in Table I and examples of powder x-ray diffraction patterns are shown in Figs. 3(a)–3(c). It is clear that the MIP reactor is effective for the formation of Ga, Ti, and V nitrides using an ammonia MIP. The x-ray diffraction patterns indicate a good level of phase purity and reaction times are shorter than those typically quoted for conductive heating techniques. In the only other comparable MIP study a commercial single mode microwave applicator (2.45 GHz, 1.2 kW) was employed to prepare bulk samples of TiN from TiO_2 over a period of 24 h, with an intermediate grinding after 12 h, and a similar but unspecified time was also required for GaN formation from Ga_2O_3.[16]

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