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Dimer arsenic source using a high efficiency catalytic cracking oven for molecular beam epitaxy

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The cracking efficiency of a catalytic double-oven arsenic dimer source has been studied by modulated beam mass spectrometry and the catalytic activity of several materials investigated through the cracking of the tetramer molecules produced from crystalline arsenic with a pyrolytic boron nitride (*p*BN) oven. The catalytic activity decreases as follows: Pt, Pt-Rh > Re > Ta > Mo, W-Re > graphite > *p*BN. Platinum and its alloys with rhodium react with arsenic above 500 °C giving definite compounds and therefore cannot be used as a catalyst. A 95% conversion efficiency is obtained with rhenium around 700 °C, a temperature which is more than 300 °C lower than the temperature required with graphite for an equivalent efficiency. Such a decrease of the operating temperature of the cracker cell is of great practical interest because of the reduction of the arsenic flux contamination by outgassing impurities.

Many authors have shown that group V dimer sources do offer noticeable advantages compared to standard tetramer sources in the growth of III-V semiconductors by molecular beam epitaxy (MBE). For instance, when using As_2 instead of As_4, the photoluminescence efficiency[1] increases while the concentration of M_1, M_3, M_4 deep levels, characteristic of MBE grown GaAs, and the recombination velocities at GaAs/GaAlAs interfaces decrease.[2,3] It has been also reported that the use of dimer species lowers gallium originated morphological defect density.[4] The simplest way to produce As_2 is to crack As_4 using a double-oven source with a cracking oven working between 900 and 1100 °C.[5,6] Recent work by Lee *et al.*[7] has shown that the thermal dissociation of the tetramer molecules As_4 is kinetically limited and that the chemical equilibrium cannot be reached in the 900–1100 °C temperature range without a catalytic effect in the cracking oven. The catalyst is either a material introduced in the cracking oven (Ta, Mo, ...) or the oven material itself (silica, graphite). Until now, the second choice has been generally retained and the ovens have been fabricated mostly from graphite. Unfortunately, the outgassing of this material at a high temperature induces an unintentional contamination of the resulting As_2 flux and consequently the epitaxial layers.[1] Therefore, pyrolytic boron nitride (*p*BN), which is widely used in standard effusion cell technology, is chosen in the fabrication of cracker ovens despite its poor catalytic activity. It is then necessary to introduce a catalyst in the source's upper zone to favor high dimer yields in the 700–1000 °C temperature range. There is only a limited amount of published studies concerning the choice of the catalysts of this reaction. To our knowledge only one attempt has been made to investigate several materials (*p*BN, graphite, Mo, Ta) as catalysts for arsenic tetramer molecule cracking.[7] However, the experiments described here are not clear. In particular no detail was given on the technique used to measure the cracking efficiency of the different materials tested. In fact, only modulated beam mass spectrometry (MBMS) allows one to obtain an accurate measurement of the source-emitted species.[8,9] The aim of this work is to study by MBMS analysis the catalytic activity of different materials: *p*BN, graphite, Ta, Mo, W-Re (26%), Re, Pt, PtRh, in an all *p*BN double-oven cracker cell.

The cell consists of two parts: a sublimator, similar to a classical effusion cell, and a cracker stage containing a series of baffles which ensure numerous molecular wall collisions (Fig. 1). The catalyst was introduced in the cracker cell's

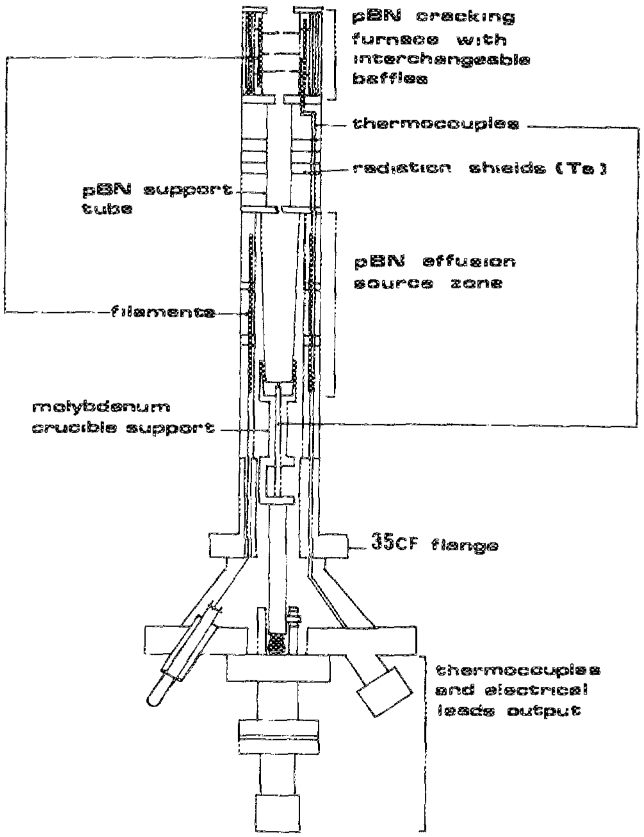

FIG. 1. Drawing of the *p*BN cracker cell used to study the catalytic activity of the different materials tested in this work.

upper zone in the form of wire or baffle. The two zones are radiatively and conductively isolated by tantalum shields and by the length of the *p*BN tube, respectively (see Fig. 1). Traditional problems of heat transfer and insulation are resolved with this design: i.e., when the cracker stage is heated at 1000 °C, the temperature is stabilized at 240 °C in the lower zone (Fig. 2), the arsenic flux being negligible at this temperature. The cracker temperature is measured by a tungsten-rhenium thermocouple positioned as indicated in Fig. 1. The tetramer to dimer cracking efficiency versus the temperature of the cracker stage was determined from the MBMS measurements in a vacuum chamber with a residual pressure below 10^{-8} Torr. The molecular beam is chopped by a rotating six-blade disk driven by a synchronous motor (60 Hz). This system provides a chopped arsenic beam at the frequency of the power driving motor. The quadrupole mass spectrometer head (ISA Riber SQS 156, 0-1000 amu) is positioned in the axis of the molecular beam. The distance between the cell aperture and quadrupole head is 120 mm as in a standard MBE 32 system. The modulated signal current from the spectrometer is processed by lock-in detection. In all experiments the temperature of the lower zone, which determines the total arsenic flux, was kept constant whatever the catalyst used (300 °C corresponding to an As_4 beam equivalent pressure around 10^{-6} Torr).

The $As_4 \Rightarrow As_2$ conversion efficiencies of various materials as a function of the cracker temperature are reported in Fig. 3. Below 400 °C, the molecular beam is essentially composed of tetramers. Among all the catalysts investigated in this study, the highest catalytic activity is obtained with platinum and platinum-rhodium alloys, which show a 32% conversion rate at 500 °C. This corroborates the well-known high catalytic activity of these materials. Unfortunately platinum reacts with arsenic above 500 °C yielding definite compounds such as $PtAs_2$ and, therefore, cannot be used as a catalyst above this temperature. A cracking efficiency of 95% is respectively obtained around 700 and 850 °C for rhenium and tantalum catalysts. Tungsten-rhenium (26%) and molybdenum exhibit a lower cracking efficiency (either in *p*BN or a graphite oven). Maximum cracking efficiencies for these materials were obtained in the 900–950 °C temperature range. All these metals produce higher cracking efficiencies than pure graphite which gives a 95% of conversion efficiency between 1000 and 1100 °C (Fig. 3). At these temperatures, it has been shown that the graphite cracker furnace causes carbon contamination of the epitaxial layers. Finally, the arsenic dimer-tetramer ratio achieved from the catalyst-free *p*BN cracker cell reaches only 0.5 at 1100 °C, thereby confirming that a *p*BN cracker cell without catalyst is not an efficient solution for the arsenic tetramer cracking reaction.[7] This result is in contrast to that observed in arsine cracking.[10] On the other hand, an important parameter which should be taken into account to achieve complete tetramer dissociation, is the pressure in the cracker stage. Indeed it is obvious from thermodynamics that an increase of pressure leads to a reduction in the efficiency of the dissociative reaction. In a previous study, Huet *et al.*[1] have verified that in a graphite furnace working at 1000 °C the cracking efficiency decreases drastically from 95% at 5×10^{-7} Torr to 70% when the pressure reaches 10^{-5} Torr. In contrast, rhenium catalysts which show a high catalytic activity retain

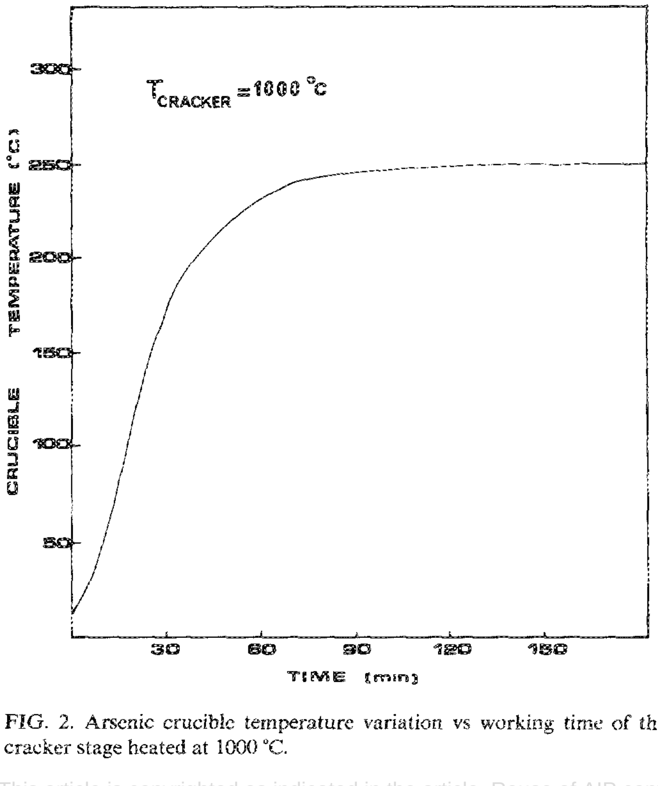

FIG. 2. Arsenic crucible temperature variation vs working time of the cracker stage heated at 1000 °C.

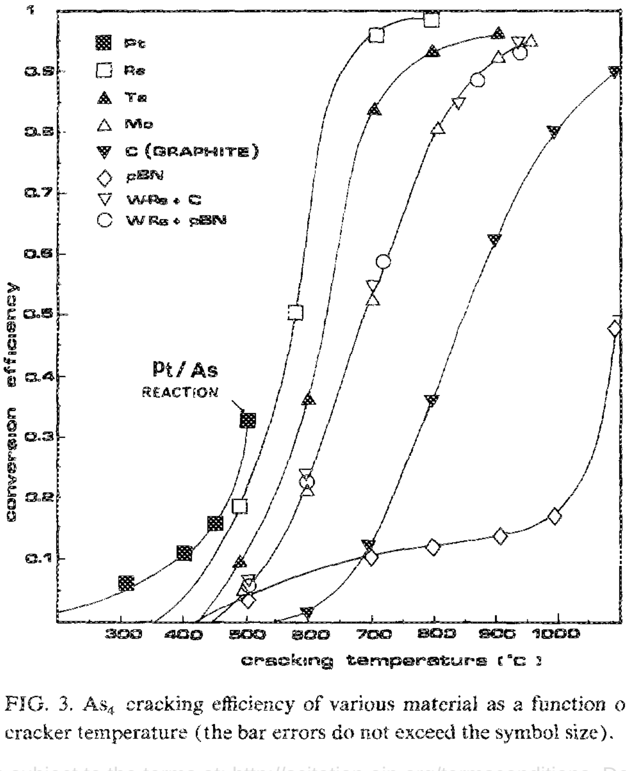

FIG. 3. As_4 cracking efficiency of various material as a function of the cracker temperature (the bar errors do not exceed the symbol size).

a 95% conversion efficiency in these conditions of pressure and temperature.

In summary, the cracking efficiency of a catalytic double-oven source for dimer arsenic generation has been studied by modulated beam mass spectrometry. The catalytic activity of the tested materials decreases as follows: Pt, Pt-Rh > Re > Ta > Mo, W-Re > graphite > *p*BN. This work confirms that the pyrolytic boron nitride is catalytically inactive in the cracking of tetramer arsenic molecules and therefore cannot be used below 1200 °C without adding a catalyst. Platinum being unusable because of its reaction with arsenic, rhenium gives the higher catalytic efficiency in the tetramer-dimer molecule conversion. Compared to a conventional graphite source, it allows one to obtain a 95% cracking efficiency for a temperature more than 300 °C lower.

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