Shock Synthesis of GaAs

by Alan R. Miller*, Jemmy Hao*, Allen Gehris J.*, and Patrick Wolf*

Explosive shock processing has been used as a tool for the synthesis of the compound GaAs starting with an elemental mixture of Ga and As powders. X-ray diffraction analysis of the shock synthesized product showed no presence of the starting material.

1. INTRODUCTION

GaAs semiconductors can operate at higher temperature and higher frequencies than Si semiconductors. However, it is difficult to fabricate GaAs because, unlike Si, it is a compound rather than simply an element. Therefore, the common fabrication techniques such as Czochralski crystal pulling and zone refining cause trouble with GaAs since the two elements diffuse at different rates. On the other hand, methods such as chemical vapor deposition and ion beam epitaxy which are not dependent on diffusion rate are very expensive. As a result, GaAs is also very expensive, about the price of gold. A further complication occurs in the conventional synthesis of GaAs because an overpressure of As gas is provided. Thus, the resulting GaAs is arsenic rich so it is an N-type semiconductor.

Explosives shock synthesis is relatively inexpensive and hence appear to be an attractive method for novel materials such as GaAs. Furthermore, it is possible to change the ratio of Ga to As or even add other elements when powders are mixed to produce either arsenic-rich or gallium-rich GaAs. The latter, of course, will be a P-type semiconductor. Several other compounds have been made by using explosive shock synthesis as an processing tool. Some examples are Ni_3Al[1], $TiAl_3$[2], WC[3], and TiC[3].

Explosives were used to propel a steel flyer plate into capsules (containing elemental power mixtures) held in a steel fixture. The kinetic shock energy causes a chemical reaction between the Ga and As powders.

Received on February 8, 1988
*Center For Explosives Technology Research
New Mexico Institute of Mining and Technology
Socorro, New Mexico 87801, USA

Two potential problems were considered while loading the capsules : 1) Arsenic powder easily oxidizes in moist air and 2) the melting point of Ga is just above room temperature. Therefore the powders were mixed under an Argon atmosphere.

GaAs compound formed by explosive shock synthesis is polycrystalline, hence it can not be used directly as a semiconductor. However, it can be used as raw material in the fabrication of single crystal GaAs. Alternatively, semiconductor substrates and solar cells are other potential areas where polycrystalline GaAs may find application.

2. EXPERIMENTAL

2. 1 Powder Preparation and Loading

The experiments were performed with 99.99% pure Arsenic and 99.999% pure Gallium mixed in powder form. While these materials are not pure enough to produce high-quality semiconductors, they are suitable for demonstrating the method of shock synthesis. Arsenic was received as −325 mesh (<44 μm) powder, while elemental Ga was obtained in ingot form. Because the melting temperature of Ga is just above room temperature, it was cooled with liquid nitrogen to make it brittle enough for grinding in a sapphire mortar. The ground Ga (−270 mesh (<53 μm)) was stored overnight at 4℃ with Drierite desiccant to remove water absorbed during grinding.

Stoichiometric quantities of the elements were mixed in a ball mill roller for 50 min. The powder container was embedded in dry ice to keep the mixing temperature below 25℃. The powder was then loaded into stainless steel capsules, shown in cross section in Figure 1. The diameter of the powder chamber is 12mm, the height is 5mm, and the inside volume is 0.56 cm^3. The powders were packed at densities of 50, 60,

Table 1 Parameters for each shot.

shot sample #		Starting Materials	Packing Density	Flyerplate Velocity km/sec	Kinetic Energy kJ
shot 1	1	Ga, As powders	80 %	1.3	18.5
	2	Ga, As powders	90 %		
shot 2	1	Ga, As powders	70 %	1.5	35.5
	2	Ga, As powders	80 %		
	3	5% GaAs+elemental Ga, As	80 %		
shot 3	1	Ga, As powders	60 %	2.0	63.2
	2	Ga, As powders	70 %		
	3	Ga, As powders	80 %		
shot 4	1	Ga, As powders	60 %	2.5	98.7
	2	Ga, As powders	70 %		
	3	Ga, As powders	80 %		
shot 5	1	Ga, As powders	70 %	2.0	63.2
	2	Ga, As powders	51 %		
	3	GaAs powder from shot 3	80 %		
shot 6	1	Ga, As powders	60 %	2.0	63.2
	2	Ga, As powders	60 %		
	3	Ga, As powders	50 %		

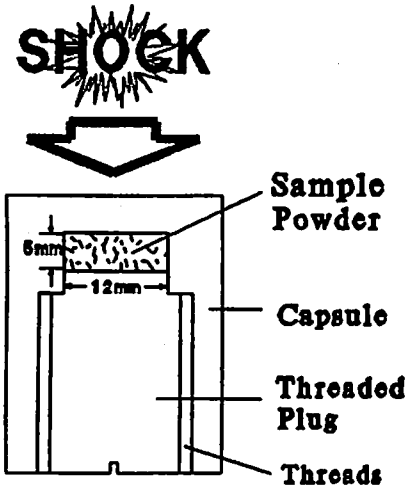


Fig. 1 The sample capsule.

70, 80, and 90% by static pressing. The relatively high packing density of 90% is possible because of the easy deformability of gallium at room temperature.

Arsenic powder upon exposure to air, can oxidize and gain as much as 70% weight in one day. Hence, the loading was carried out in an argon atmosphere at a temperature below the melting point of gallium. The capsules were fastened tight and sealed with wax before removal from the glove box. They were then stored in dry ice until the time of the test. The explosive shock synthesis was generally performed within 24 hours of loading. The parameters such as starting materials, packing densities, flyer plate impact velocity, and kinetic energy for each shot are listed in Table 1.

2. 2 Shock Set-up

The energy for shock synthesis is provided by the impact of a steel flyer plate accelerated to a velocity of about 2 km/sec using a high explosive. Two different methods were used to create the plane wave, viz., mouse trap assembly and conical lens.

2. 2. 1 Mousetrap method

With the mousetrap method (Figure 2), the point-source detonation is transformed into a line wave by a triangular explosive sheet that is perforated in a special way[4]. It is placed on top of the

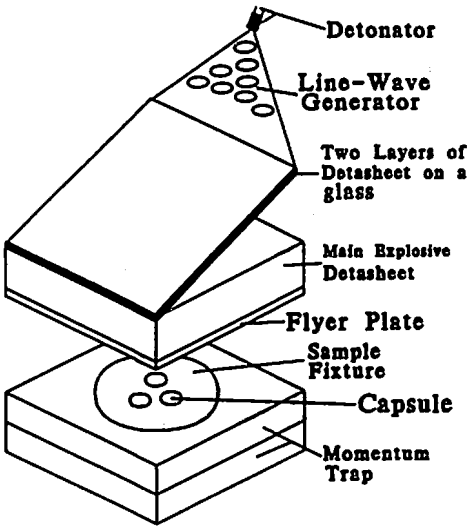


Fig. 2 The "mouse-trap" shock assembly.

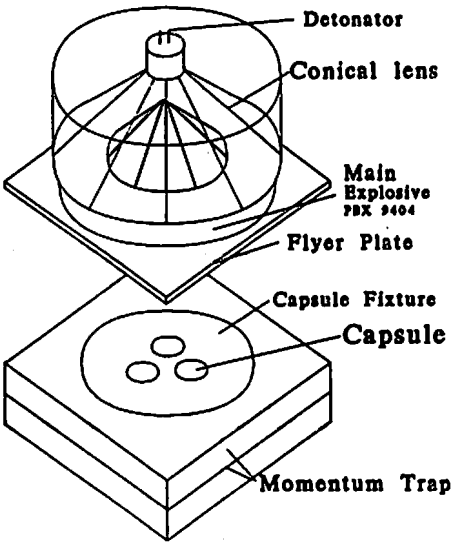


Fig. 3 The conical explosive lens shock assembly.

whole assembly. Then the line wave from the detonation is converted to plane wave by a sheet explosive mounted on an inclined piece of glass (Figure 2). As the line wave propagates, the glass is fractured and the glass fragments are driven downward into the main detasheet explosive. Since the glass plate is oriented at an angle to the main explosive, all the glass fragments reach the main explosive at the same time to produce a plain wave. This propels the steel flyer plate towards the samples contained in the target assembly. There were three capsules in each sample fixture (Figure 2). A momentum trap beneath the samples were used to reduce reflection of tensile waves back into the samples.

2. 2. 2 Conical lens method

Plane shock waves were also produced with a conical lens (Figure 3). In this design, two cones and two explosives with different velocities are used. The slower explosive is placed inside the inner cone, while the faster explosive is placed between the two cones. Detonation starts at the apex.

The shock front from the faster explosive moves down the side as the front from the slower explosive moves down the interior. If the shape is correctly chosen, a planar shock wave will arrive at the base of the cone, and then initiate the main explosive, PBX 9404 (Figure 3). This method produces more nearly planar waves than the mousetrap method. Plane waves are important because they ensure uniform pressures and temperatures. Both designs have been used successfully for other shock experiments.

Six shots containing a total of 17 samples were performed (Table 1). Flyer plate velocities ranged from 1.3–2.5 km/sec. This resulted in the kinetic energy input in the powders ranging from 18.5–98.7 kJ. The necessary amount of main explosives was calculated by Gurney's equatiodn[5]. The stand-off distance between flyer plate and sample fixture is calculated by an empirical formula[6]. The shocked samples were analyzed by X-ray diffraction, optical microscopy, specific gravity, and scanning electron microscopy.

3. RESULTS AND DISCUSSION

The capsules were cut open with a water-cooled lathe to recover the consolidated samples for analysis.

3. 1 X-ray Diffraction

X-ray diffraction analysis was performed both before and after shock loading to verify the extent of reaction. X-ray diffraction patterns of the samples from the first two shots showed the presence of GaAs as well as Ga and As indicating only partial reaction. Furthermore, the diffraction pattern revealed that GaAs was present only at the rear (non-impact) part of the sample. This means that the shock wave transfers higher energy to the powder in the bottom part of the capsules.

All experiments after shot 3 used a higher kinetic energy and therefore produced a higher yield of GaAs. The diffraction patterns are shown in (Figure 4a-d). Pattern (d) was obtained from a commercial sample

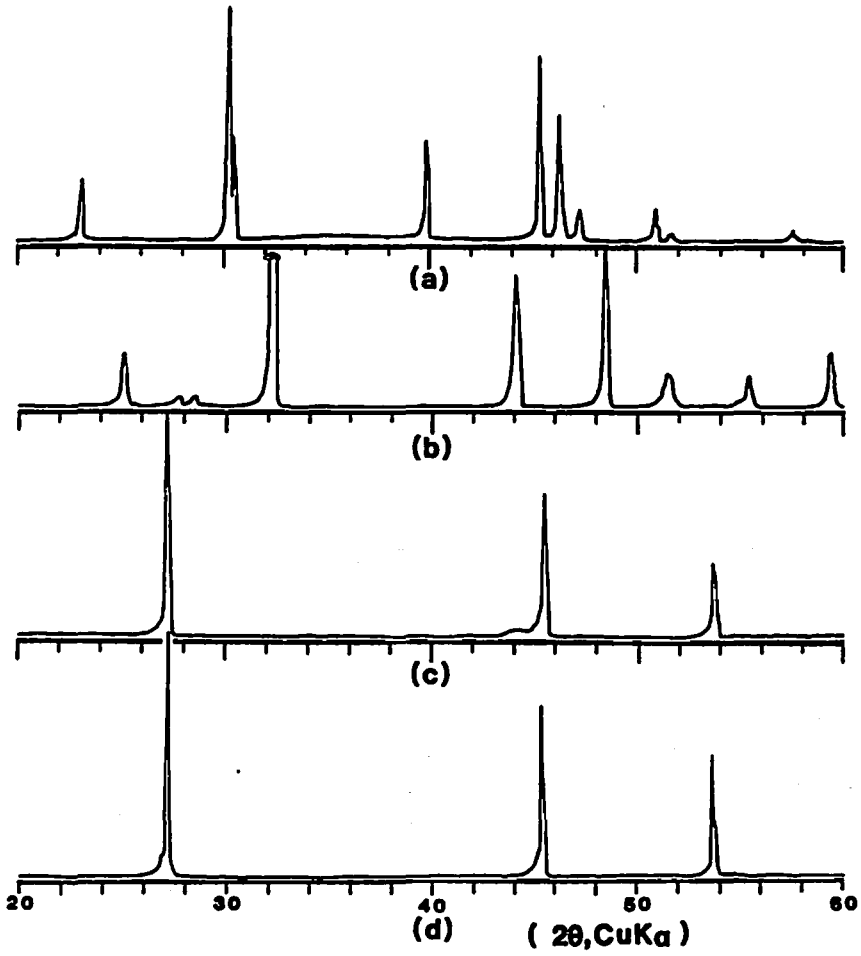


Fig. 4 X-ray diffraction patterns of (a) Ga, (b) As, (c) shock-synthesized GaAs and (d) commercial GaAs.

of GaAs, while pattern (c) was made from one of our shocked samples. Notice that the two patterns match except that the peaks of the shocked sample are broadened. The peak-broadening effect was more apparent on Debye-Scherrer photographic film than on the diffractometer chart.

The X-ray diffractometer was calibrated to determine the sensitivity of the instrument by analyzing mixtures of As and GaAs. It was found the minimum amount of As that can be detected in a GaAs sample is 12 wt.%. Thus it can be inferred from the results that more than 88% of elemental Ga and As converted into GaAs.

3. 2 Optical Microscopy

Samples were mechanically polished and etched for 10 seconds with a solution of water, hydrogen peroxide, and sulfuric acid (8 : 1 : 1). Photomicrographs of

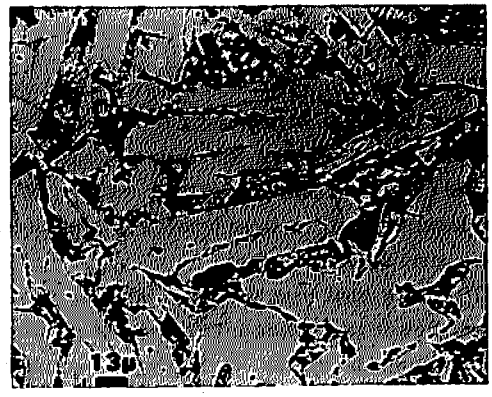
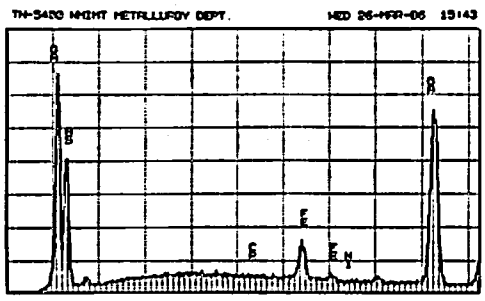
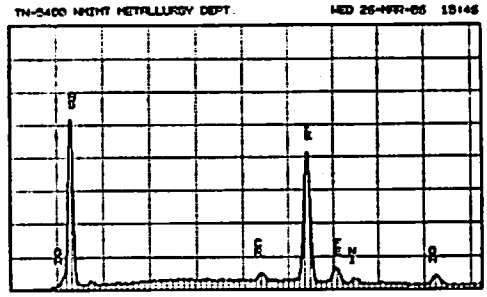


Fig. 5 Optical micrograph of GaAs sample.

the samples (Figure 5) show lathlike grains with dendritic regions and dark areas between the lath structure. Also, this analysis shows that samples with higher initial bulk density (70%) appear the same as

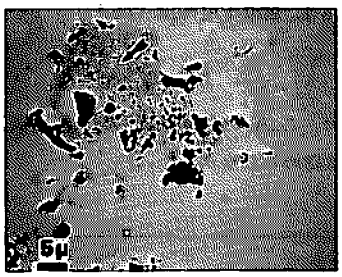


EDS on spot A



EDS on spot B

Fig. 6 Scanning electron microscopy and EDS on spots A and B of a sample.



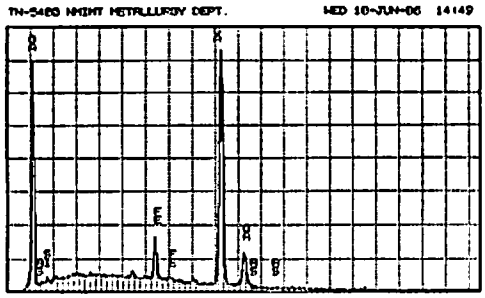


Fig. 7 SEM and EDS showing Ga-rich region.

those with lower densities (60% or 50%). The best samples were produced by the parameters of shot 3, 5, and 6.

3. 3 Specific Gravity Measurements

Specific gravity of the shocked synthesized GaAs was determined by water displacement to be 4.7-5.1 g/cc. The theoretical density of GaAs being 5.31 g/cc.

3. 4 Scanning Electron Microscopy

Samples were repolished but not etched to reduce surface relief for SEM observation. Elemental analysis by EDS shows that the grain-boundary region (spot B) is As rich (Figure 7). Also a trace amount of Fe and Cr, presumably from the sample capsule, is seen in this region.

In general, the EDS results showed that samples with high initial packing density result in unequal distribution of reactants during shock loading. Near the center of the sample with 80% packing density, some unreacted Ga was found (Figure 8), squeezed toward the central region of the capsule.

4. CONCLUSIONS

The results of this work show that GaAs can be synthesized from the elemental constituents by explosive shock processing. The optimum flyer plate velocity was found to be 2.0 km/sec, which resulted in non-porous compacts. Also the initial packing density of powders should not exceed 70%, to obtain maximum yield of the reaction product.

5. ACKNOWLEDGMENT

This work was performed through the research program of the Center for Explosives Technology Research (CETR) of New Mexico Institute of Mining and Technology. Funding was provided by the State of New Mexico Department of Economic Development and Tourism.

6. REFERENCES

1) Graham, R. A., Morosin, B., Horie, Y., Venturini, E.L.,Boslough, M., et al. 1986. In Proc. 1985 Am. Physical Soc. Topical Conf. on Shock Waves in Condensed Matter, Spokane, Washington, July 22-25, 1985, ed. Y. Gupta.
2) Shock Waves in Condensed Matter, ed. by Horie, Y., Hoy, D. E. P., Simonsen, I., Graham, R. A., Morosin, B., American Institute of Physics, New York, 1986.
3) Batsanov, S. S. 1978, chemical reaction under the action of shock compression. p.288 in Detonation Critical Phenomena : Physicochemical Transfor mations in Shock Waves, ed. by F. L. Dubovitskii, UCRL-Trans. 11444, Lawrence Livermore National Laboratory.
4) "Shock Waves and High-Strain-Rate Phenomena in Metals", ed. by Marc A. Meyers and Lawrence E. Murr, Plenum Press, New York, 1981, p.350.
5) Pro. of the 12th Annual Symposium, "Behavior and Utilization of Explosives in Engineering Design", Albuquerque, New mexico, March 2, 1972, p.117.
6) "Shock Waves and High-Strain-Rate Phenomena in Metals", ed. by Marc A. Meyers and Lawrence E. Murr, Plenum Press, New York, 1981, p.369.

GaAsの衝撃合成

by Alan R. Miller, Jemmy Hao, Allen Gehris J., and Patrick Wolf

GaとAsの混合粉末を原料として，爆発衝撃処理の手法により，GaAsの合成を試みた。回収試料のX線回折では，GaAsのピークのみが現れ，出発原料のピークは認められなかった。