

Growth of Fe and FeAs₂ Films on GaAs by Organo-Metal Chemical Vapor Deposition Using Pentacarbonyl Iron and Arsine

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ABSTRACT

A number of iron and iron arsenide films have been grown using pentacarbonyl iron and arsine by conventional organo-metal chemical vapor deposition (OM-CVD) on single-crystal GaAs. Auger sputter profile on a 1240Å-thick iron arsenide sample gave a composition consistent with the intended compound, FeAs₂, a narrow-gap semiconductor. Infrared transmission data on the same film yielded an optical gap of 0.16 ± 0.01 eV, which compares with the known electrical gap of 0.22 eV for bulk FeAs₂. An apparent catalytic action of pentacarbonyl with arsine allows the iron arsenide to form from arsine at low temperatures near 300°C. The low temperature of growth suggests the possibility of forming heterostructures between a narrow-gap semiconductor and a ferromagnetic film. Such a structure was successfully grown on GaAs.

Recent work by Prinz and Krebs (1) has shown that high quality epitaxial Fe can be grown on GaAs surfaces for film thicknesses less than 1 μm. These thin epitaxial films were deposited by the molecular beam epitaxy (MBE) technique using high purity elemental Fe as the source. In those experiments, the optimum growth conditions, as determined by reflection high energy electron diffraction and ferromagnetic resonance occur for substrate temperatures between 175°-225°C.

More recently, Kaplan and Bottka (2) have shown that high quality epitaxial Fe on GaAs surfaces can also be grown using chemical vapor deposition (CVD) by decomposing the organo-metal (CO)₅Fe thermally on the substrate at 200°C in an ultrahigh vacuum chamber. In that UHV-OM-CVD process, *in-situ* Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) analysis was used to characterize the growth process of the Fe film. Those studies showed that Fe growth on GaAs proceeds by layer rather than island formation. The LEED data elucidated the nature of the atomic arrangement of Fe on GaAs for various surface orientations for the first few monolayer coverage.

In the present work, we investigated the growth of films of iron and one of its compounds, the narrow-gap semiconductor FeAs₂, on GaAs by the more conventional technique of OM-CVD, which uses H₂ as a carrier gas to transport the OM species to the substrate. The conventional technique is simple, efficient, and amenable to large scale application.

We have found that with care normal OM-CVD technique does allow the production of Fe and FeAs₂ films on GaAs. Indeed, to our knowledge, this study has produced the first synthesis of FeAs₂ in thin film form. This synthesis is apparently aided by a catalytic enhancement of the decomposition of the arsenic source (AsH₃) in the presence of the iron source, pentacarbonyl iron (CO)₅Fe, which allows FeAs₂ to be formed at a relatively low substrate temperature.

Experimental

The vertical OM-CVD reactor used in these experiments (Fig. 1) is a conventional setup used to grow high quality GaAs and AlGaAs/GaAs on GaAs substrates but with the addition of the (CO)₅Fe source added to the manifold. The reactor gas manifold and mixing system were constructed from passivated stainless steel tubing. Parts were either welded or joined with vacuum-compatible VCR fittings. The system utilizes mass flow controllers for control of the various gaseous flow rates and pneumatically controlled bellow valves for switching all gaseous flows.

The carrier gas used was ultrahigh purity, palladium-purified hydrogen. The arsenic source was ultrahigh pu-

rity arsine contained in a commercially supplied high pressure cylinder. The 99.5%-grade (CO)₅Fe from Alfa Ventron was twice vacuum distilled and transferred into a stainless steel cylinder/bubbler which was held at 24°C during growth. All saturated vapors and gases were mixed and diluted with H₂ in a manifold prior to introduction into the reactor.

The GaAs substrates were undoped liquid-encapsulated Czochralski (100) oriented wafers which were bromine-methanol polished, cleaned, and etched in 1:1 NH₄OH:H₂O prior to loading into the reactor.

The cold-walled growth vessel was a quartz cylinder coupled to the manifold with ultratorr fittings. The sample rested on a silicon carbide-coated graphite susceptor and was RF inductively heated.

Growth of Fe Films

Typical growth conditions for Fe on GaAs are shown in Table I. Iron films grow easily in the temperature range 150°-300°C, and the optimum temperature is at 200°C. This is similar to that found in MBE and in UHV-OM-CVD experiments. The growth rate depends upon the partial pressure of (CO)₅Fe in the reactor. For typical flows of 15 cm³/min of hydrogen through the (CO)₅Fe bubbler and 1 l/min of H₂ dilution, the growth rate was about 200 Å/min, as determined from Dektak measurements.

The sample temperature and its surface IR emissivity was monitored during growth with an Iacon pyrometer¹ operating in the 2-2.6μ spectral range. At 200°C, and just prior to growth, the value of the GaAs substrate emissivity was 0.7. Upon initiation of growth, this value dropped to 0.29, indicating the formation of a metallic, infrared reflecting film. The grown Fe films are highly reflective (Fig. 2), show no indication of tarnishing with time, and are very strongly bonded to the GaAs substrate. A total of 15 Fe/GaAs samples were grown.

Growth of FeAs₂ Films

There are a number of compounds which can be formed between iron and arsenic, including Fe₂As, FeAs, and FeAs₂. The last compound, iron di-arsenide, appears naturally as the mineral loellingite (3), and its growth is favored by an arsenic-rich environment during formation. It is a narrow-gap semiconductor whose properties have been partially studied.

Bulk FeAs₂ has been grown (6) by the vapor transport method in the temperature range 600°-800°C, but, to our knowledge, thin film FeAs₂ had never been previously synthesized. FeAs₂ has the cell dimension (4-7) of $a = 5.300\text{Å}$, $b = 5.983\text{Å}$, and $c = 2.882\text{Å}$, an enthalpy of formation of 10.4 kcal/mol (8, 9), specific gravity of 7.4 (10), and is diamagnetic (11, 12).

¹ Iacon Radiation Thermometer Series 300 C, manufactured by Iacon, Inc., Niles, IL 60648.

Key words: semiconductor, CVD, heteroepitaxy.

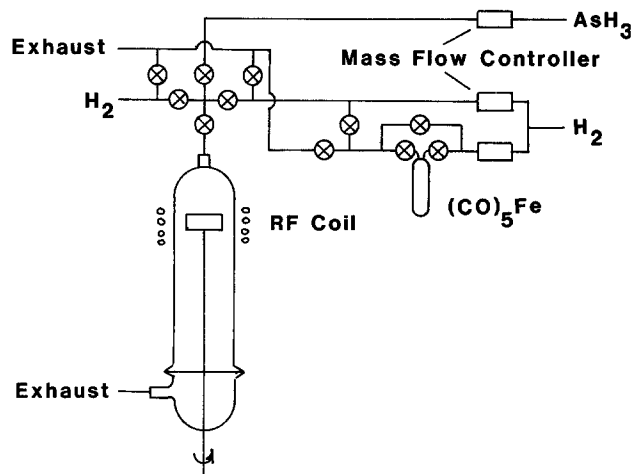


Fig. 1. OM-CVD system used in the growth of Fe and FeAs₂ on GaAs. Arsine and hydrogen enter from tanks located to the right and are exhausted through a bubbler and a burner (neither shown) to the left. The substrate is rotated at approximately 30 rpm.

Table I summarizes the growth conditions of FeAs₂ on GaAs. These films grow in the temperature range 200–400°C, and the optimum growth temperature seems to be near 300°C, considerably below the vapor transport temperature used for bulk growth (6). We believe that the low temperature growth of FeAs₂ in our OM-CVD system may result from a catalytic action of Fe or (CO)₅Fe on the decomposition rate of AsH₃. Schlyer and Ring (13) have observed pyrolytic decomposition of (CH₃)₃Ga and PH₃ over product-crusted walls at 240° and 270°C. On the basis of their analysis, the authors propose that AsH₃ and (CH₃)₃Ga can catalytically decompose at low temperatures on GaAs surfaces after surface adsorption and formation of complexes. A similar surface catalysis may be operable in our case.

The grown films are highly reflective, and their emissivity during growth is about 0.7, similar to GaAs and distinctly different from the surface emissivity of the growing iron films. The high emissivity is consistent with the low diffuse reflectivity of loellingite (14). The iron di-arsenide films have low surface conductivity, are soft, and show no signs of degradation after nine-month exposure to the atmosphere.

X-ray diffraction measurements at grazing incidence was attempted to obtain crystallographic information about the thin FeAs₂ film. However, results were inconclusive due to the strong background signal of the GaAs substrate.

Figure 3 shows the sputter Auger profile of one of the six FeAs₂-grown films. Atomic concentration estimates from this data indicate that the preferred stoichiometry is nearer FeAs₂ rather than FeAs or Fe₂As, two other possible formations. The interface between the film and the substrate is about 80 Å wide. The Ga and carbon peak was monitored but not found in the film. The observed 20% drop in the As atomic concentration in going from FeAs₂ into GaAs is near the 23% atomic concentration difference expected between the two compounds. Interferometric

Table I. Growth condition for Fe and FeAs₂ on GaAs

	Fe	FeAs ₂
Reactor pressure (torr)	760	760
Growth temperature (°C)	150-300	200-400
Optimum growth temperature (°C)	200	300
Total gas flow (l/min)	1.0	1.1
(CO) ₅ Fe source temperature (°C)	24	24
H ₂ /(CO) ₅ Fe bubbler flow (cm ³ /min)	15	10
Arsine flow (cm ³ /min)	—	90
Growth rate (Å/min)	200	80

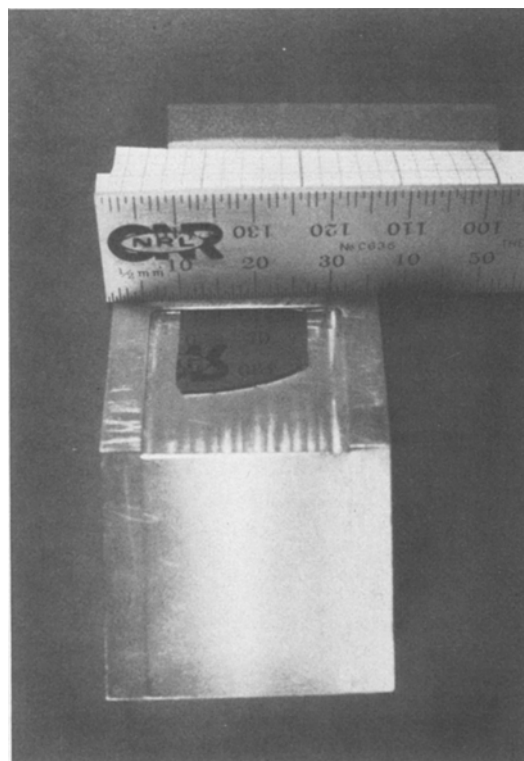


Fig. 2. Typical Fe film grown on single-crystal GaAs

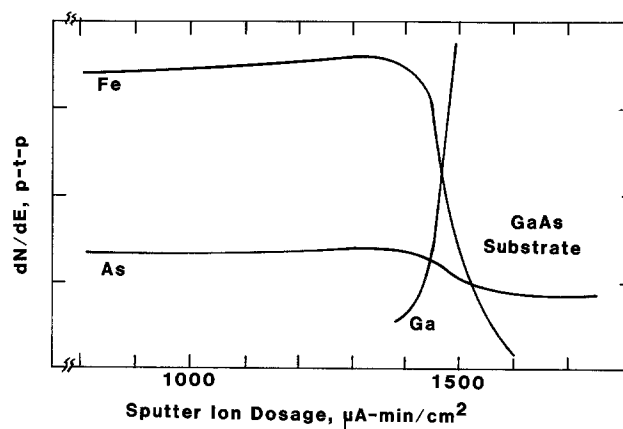


Fig. 3. Sputter Auger profile of FeAs₂-grown film. Variation of Auger elemental sensitivity factors are included. Interferometric measurement on the sputtered crater gave estimate of the film thickness and its growth rate. Film thickness is 1240 ± 50 Å.

measurements on the sputtered crater gave estimate of the film thickness and its growth rate. Matrix effects were taken into consideration in presenting the data in Fig. 3. The effect of preferential sputtering in stoichiometric ratio is not known.

Infrared transmission measurements were conducted on the grown 1240 Å film sample profiled in Fig. 3 and on a companion GaAs single-crystal substrate. Figure 4 presents the results in terms of the normalized ratio of sample transmittance to that of the substrate over the region from 3.5 to 20 μm. The electrical gap of FeAs₂ determined from the temperature dependence of a bulk sample is 0.22 eV (11) and that energy lies almost exactly at the energy where the normalized transmission has risen half way. If we define the optical gap conventionally as the energy at which the absorption coefficient is 10⁴ cm⁻¹, and neglect interference effects in the optically thin sample, the optical gap of the deposited film is 0.16 ± 0.01 eV. The observed gap energy difference of 0.06 eV between the bulk and our film stems from the different methods of determining gap energies. The bulk conductivity *vs.* temperature measurement gives the extrapolated gap energy at 0 K, whereas our optical data were

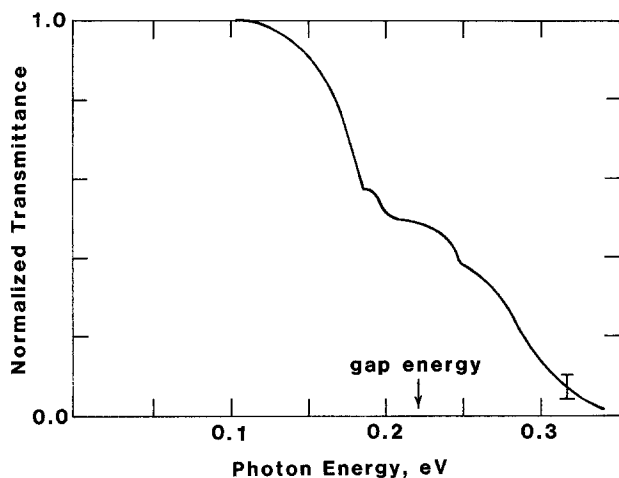


Fig. 4. Normalized ratio of sample transmittance (FeAs_2) to that of the GaAs substrate in the infrared. Arrow indicates the electrical gap energy (11) of FeAs_2 . Uncertainty in the measurement is shown by the bar at the right lower corner.

taken at 300 K. The 2×10^{-4} eV/K gap variation is close to the value observed in most semiconductors. The sample transmission data reveal repeatable optical structures within the measured range which are absent in the GaAs substrate and which appear to be real properties of the film.

Summary

Conventional OM-CVD has been used to grow high quality films of the metal Fe and one of its compounds, FeAs_2 , upon single-crystal GaAs. The successful growth of the narrow-gap semiconductor FeAs_2 raises the possibility that less well-known narrow-gap semiconductors of the type (Fe, Ni, Co)-(P, As, Sb) may be possible. In addition, the growth of compatible Fe and FeAs_2 films within the same OM-CVD system offers promise that heterostructures involving metal and narrow-gap semiconductors may be fabricated in a simple manner by OM-CVD. This possibility is accentuated by the low temperature required at which FeAs_2 grows from arsine in the presence

of pentacarbonyl iron. Because of this relatively low growth temperature, attempts were made to deposit alternate thin layers of FeAs_2/Fe on GaAs. We were successful in a preliminary growth of a $\text{FeAs}_2/\text{Fe}/\text{FeAs}_2/\text{Fe}$ heterostructure, whose overall thickness was approximately 150 Å, on single-crystal GaAs. The resulting heterostructure has a brilliant luster, and is strongly bonded and lasting. Further work is needed to characterize its properties.

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Oxygen-Doped Molybdenum Films for MOS Gate Application

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ABSTRACT

Intentionally oxygen-doped Mo films (MoO_x) for MOS gate electrodes are investigated to eliminate the penetration of implanted As ions into the silicon substrate through the gate electrodes and gate oxides. The MoO_x films are prepared by reactive sputtering of Mo in a mixture of Ar and O_2 gases. Depth profiles of As ions and MOS C-V curves are measured to estimate stopping properties. For as-deposited MoO_x films, whose oxygen concentrations are higher than 20 atom percent (a/o), As ion penetration depth is within 0.15 μm under 100 keV As ion implantation. This depth is about one third of that in normal Mo films. This excellent stopping property can be attributed to the nearly amorphous structure, which suppresses As ion channeling in the films resulting from oxygen doping. The resistivity of MoO_x films with 39 a/o oxygen after annealing at 1000°C for 30 min is 25 $\mu\Omega\text{-cm}$, which is only three times as large as that for normal Mo films. In MoO_x gate MOS structures, MOS characteristics are independent of oxygen concentrations in the films, and are almost the same as the characteristics for normal Mo gate electrodes.

Thin molybdenum (Mo) films have been attracting much attention as self-aligned gate electrodes and interconnections for highly packed MOSFET integrated circuits (1, 2). The reason for this is their low resistivity, high temperature resistance, and high density (10.3 g cm^{-3}), which is beneficial for ion implantation masking materi-

als. Nozaki, however, has reported that unwanted depletion modes have been observed in Mo gate MOSFET characteristics when arsenic (As) ion implantation is carried out using Mo gates as masks (3). Fujinaga has pointed out that the main cause of this phenomenon is the anomalous penetration of As ions into the silicon substrate caused by As ion channeling in some columnar Mo grains (4). To improve stopping properties, silicon nitride (5) and molybdenum nitride (6) coatings on Mo films, as

Key words: metals, integrated circuits, ion implantation, sputtering.