Chemical Vapor Deposition Methods for Preparation of Radioactively Doped Thin Films

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ABSTRACT

Perturbed Angular Correlation (PAC) spectroscopy is an important nuclear technique and has found a wide variety of solid state physics applications /1/. The technique requires that small amounts of radioactive probe atoms are introduced into the samples. These will interact with their surroundings and yield information about the local environment. The technique is well established and a detailed description can be found in Reference /2/. A prominent probe atom with ideal properties for the PAC method is ^{111}In, which is also very well suited for the investigation of II-VI semiconductors, as it is an effective dopant in these materials /3,4/. The main problem one has to face in doing these experiments is the radioactive doping without changing the sample properties and thus creating artefacts. Thin films offer the possibility of introducing probe atoms homogeneously in adequate amounts during their growth. However, special techniques need to be developed, as the total number of required probe atoms is only about 10^{13} ^{111}In atoms.

One of the most common techniques used to prepare thin films is the Chemical Vapor Deposition (CVD) method. Using CVD, it is possible to prepare a very large number of thin films with different compositions. The problems is to introduce the probe atoms onto the films. This study presents the design of two different methods for preparing radioactively doped thin films. The method consists of a Low Pressure Chemical Vapor Deposition (LPCVD) process, wherein the source material can be of a very wide variety, depending on the nature of the desired thin film.

CVD METHODS

The metal-organic method employs pyrolysis (thermal decomposition) of appropriate column II alkyls (e.g., diethylzinc) and hydrides of the appropriate column VI elements (e.g., H_2S). If the pyrolysis occurs on an adequately heated substrate, correct positioning will take place.

LPCVD employs a compound as one of the chemically active components (e.g., H_2S), which reacts with another reactant (e.g., Zn) to form a new compound (ZnS and H_2). If the reaction occurs in the presence of an appropriately heated substrate and at an appropriate pressure, deposition of the desired compound will occur.

The present work describes:

a. Considerations for the design of a laboratory scale CVD reactor for preparation of radioactively-doped thin films.
B. A theoretical model for chemically vapor deposited radioactively-doped ZnS.

RADIOACTIVE MATERIAL

PAC spectroscopy desires a threshold level of radioactive atoms. Since a sample with 10^{13} radioactive atoms is adequate for the PAC measurement, the basic consideration in this part of the work is to prepare a sample with radioactive dopant atoms. The following calculations show the activity and calculation of the radioactive material amount necessary for a sample preparation.

$$A = \lambda N \qquad (1)$$

where:

A – Activity
N – Number of radioactive atoms
λ – Frequency.

Since the radioactivity decays as a function of time,

$$N = N_0 e^{-\lambda t} \qquad (2)$$

where t designates time.

For half-life time:

$$0.5 = e^{\lambda t 1/2}$$

$$\lambda \cong \frac{0.7}{t_{1/2}} = 3 * 10^{-6} S^{-1}$$

where S designates seconds.

Since the predicted deposition efficiency is approximately 10%, we can assume that we need at least 10^{14} radioactive atoms to prepare a sample.

In this case the total activity of the radioactive material will be:

$$A = 10^{14} * 3 * 10^{-6} = 3 * 10^{8} S^{-1}$$

Since,

$$1 Cu = 3.7 * 10^{10} S^{-1}$$

the total activity of 10^{14} radioactive atoms is

$$A = \frac{3 * 10^{8}}{3.7 * 10^{10}} \simeq 10 \text{ mCu}$$

Since the amount of the radioactive material is very small, it is impossible to handle it in the solid state. This diminishes the possibility of using solid ^{111}In and carrying it to the reaction zone by LPCVD. One way to use the LPCVD method is to hold the ^{111}In on a carrier, which releases the radioactive atoms at a high temperature when a stream of controlled carrier gas carries the atoms to the deposition zone. The preparation of such a carrier is described in References /1/ and /2/. Generally, ^{111}In in a solution of HCl dried in a quartz tube forms $InCl_3$. The product is placed at one end of the tube while at the second end a piece of copper sheet is placed. When the copper tube is held under a temperature gradient ($T_{InCl3} < T_{Cu}$) in the presence of H_2, $InCl_3$ decomposes and In migrates to the copper sheet surface. The quartz sheet can be used in any type of thin film producer machine, when the In evaporates from the copper sheet surface and is carried with the carrier gas to the deposition area.

Since there is no data available on the preparation of radioactively doped thin films by CVD, the chances of success are not immediately clear, which leads to the first stage of this work: the design of a small diameter laboratory scale CVD reactor. The basic concept is to design an inexpensive modular CVD reactor to prove the possibility of preparing radioactively doped tin films and then to improve that reactor, if the results are positive.

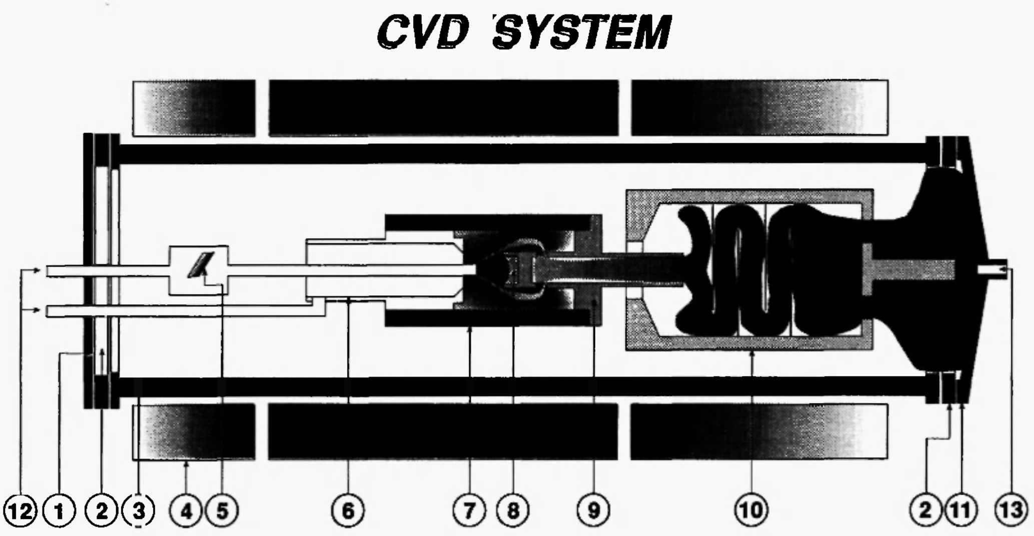
The most important issue in the design is the processing of radioactive materials. This requires the design to achieve high deposition efficiency, minimize the contaminated area and prevent radioactive materials from leaving the CVD reactor.

DESIGN CONSIDERATIONS

Figure 1 shows a general view of the designed CVD system.

The reactor is based on a stainless steel tube placed inside a 3-zone, self-controlled electrical furnace. On each side of the reactor there is a water-cooled adapter. The "inlet" cover is designed to introduce all precursors into the reaction chamber and also support the co-axial nozzle, reaction chamber and the sample holder. The sample holder also serves as the reaction chamber gas outlet.

The outlet of the reactor is connected to a vacuum system through a water-cooled adapter. In the outlet,



1. Inlet cover
2. Water cooled adaptor
3. Reactor
4. Furnace
5. Radioactive material holder
6. Co-axial nozzle
7. Reaction chamber
8. Substrate
9. Reaction chamber cover
10. Particles trap
11. Outlet cover
12. Gas supply inlet
13. Outlet

Fig. 1: CVD System

behind the water-cooled adapter, there is a center-threaded sealing ring. This ring serves as a support for a trap for solid particles that do not deposit on the substrate.

Due to radioactive material hazards, the reaction should occur solely in the reaction chamber with a very high efficiency.

To improve the efficiency, the precursors are introduced into the reaction chamber through a focused stream co-axial nozzle. The radioactive atoms are carried into the reaction zone through the central pipe of the nozzle, with carrier gas, or with one of the diluted reactants. Since the outer pipe of the nozzle ends in a cone on the inner side, the gas stream that leaves the nozzle is focused on a point near the substrate.

This stream surrounds the central stream and forces it to flow directly to the substrate. The following design guarantees the arrival of the radioactive material at the deposition substrate and its high efficiency deposition.

SIMPLIFIED SYSTEM DESCRIPTION FOR THEORETICAL TREATMENT

A central stream of carrier gas containing dopant atoms obtained by an evaporation arrangement /3/ flows into a cavity filled with carrier gas and reactants needed for a CVD deposition process. For instance, one may consider the deposition of Zns due to the reaction of Zn with H_2S /3/.

The growth rate of ZnS under conditions in which Zn or H_2S are carried into a cavity by a central stream impinging on a substrate was treated elsewhere /3/. Here we shall attempt to determine the distribution of dopant in the growing ZnS when a central stream containing an initial concentration of Cd_o is introduced steadily into the reactor cavity in addition to the reactants (Zn and H_2S).

We shall consider the case of a substrate with spherical geometry.

DOPANT CONCENTRATION IN THE GROWING SAMPLE

The dopant flows toward the surface in a jet (stream) of carrier gas. In the reactant cavity some dopant leaves this jet due to mixing and diffusion. The cavity is filled with a flowing gas phase of reactants and carrier gas. This gas phase flows at a velocity $\overline{V}$, lower than the velocity of the jet. Thus dopant reaches the growth substrate due to the flow of the gas phase in the cavity (phase flow) and the flow of the jet. The velocity components of the jet in a spherical geometry near the substrate are /3/:

- $V_f = ar$
- $V_z = -2az$

where a is a constant, r is the distance of a point from the symmetry axis and z the vertical distance from the summit of the sphere.

The rate of dopant Q_s arriving at the substrate surface due to the flow of the jet is, therefore:

$$Q_s = Cd_o a\sqrt{r^2 + 4z^2} \qquad (3)$$

The total amount of dopant supplied to the surface of the substrate per unit time should include the contribution of the phase flow:

$$Q_{total} = Cd_o a\sqrt{r^2 + 4z^2} + Cd_o \eta V \qquad (4)$$

where η is a parameter expressing the mixing process between the jet and the flowing gas phase in the reactor cavity.

Assuming that the dopant mass supply is the process limiting step, integration over time of Eq. (4) yields the amount of dopant m present in the substrate at various locations:

$$m = m_{min} + \frac{m_{min}}{\eta \overline{V}} a\sqrt{r^2 + 4z^2} \qquad (5)$$

Here m_{min} is the minimum amount (at the summit of the sphere) of dopant per unit area of substrate deposited after a time τ.

$$M_{min} = V Cd_o \eta \tau \qquad (6)$$

One can conclude, therefore, that samples with various dopant concentrations can be obtained from growth on spherical substrates. The amount of dopant can be further regulated by controlling the time of growth, phase flow velocity V (carrier gas flow rate) and reactor geometry, which influences both the value of parameter a and phase flow velocity.

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