THIN GE:C:H FILMS DEPOSITED FROM ORGANOGERMANIUM COMPOUNDS WITH THE USE OF RADIO FREQUENCY PLASMA

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A b s t r a c t. Plasma deposition of thin Ge:C:H films from tetramethyl- and tetraethylgermanium in a parallel-plate radio frequency (RF) reactor is presented. Films deposited at W/FM values below 0.6 GJ/kg are transparent, soft and insulating materials, forming polymer-like layers. Materials deposited at W/FM over 0.8 GJ/kg form dense, hard, black in colour semiconducting films. DC conductivity and optical gap measurements show a substantial tunability of these materials' physical properties (conductivity in the range of 10^{-12} to 10^{-2} S/m and optical gap in the range of 1.2 to 3.2 eV). Results of structural studies, comprising FTIR and ^{13}C CP MAS NMR measurements, strongly indicate an organometallic character of the polymer-like films and suggest a much more inorganic structure for the semiconducting materials. Applications for the discussed materials are proposed, namely in the thermistor technology as well as in the manufacture of amorphous superlattice systems.

K e y w o r d s: thin films, organogermanium compounds, high frequency glow discharge.

INTRODUCTION

An interest in the fabrication of materials composed of mixed fourth group elements (IV-IV) is bound to the desire of synthesizing substances characterized by the tailor-cut values of their bandgap width. Out of pure IV group elements, the first three can crystallize in the cubic form, making use of covalent sp^3 bonds, and their respective bandgap widths amount to:

- for diamond   –   5.50 eV
- for silicon   –   1.12 eV
- for germanium   –   0.67 eV

As far as two-component IV-IV systems, comprising the above elements, are concerned, two of them are well known. One is silicon carbide (SiC), a stoichiometric compound, whose cubic form has the width of the bandgap equal 3.0 eV [1], and the other is a series of solid solutions of silicon and germanium of the bandgap width values ranging between 0.65 and 1.4 eV (for crystalline materials) [2]. When it comes to a germanium/carbon system, however, it does not

comprise any thermodynamically stable phase [3]. A stoichiometric compound, germanium carbide, is not known at all, and every attempt to formulate a solid solution fails because of a tremendous difference in melting points of carbon and germanium [4]. Under these circumstances, the ways to manufacture such a system are limited to PVD/CVD methods, with the material being deposited in a form of a thin film.

In the case of plasma-assisted PVD and CVD methods, the following ones are well suited for the deposition of Ge:C types of films:

- Sputtering of mixed germanium/carbon target in the atmosphere of inert gas: PVD - hydrogen free Ge:C films [5]
- Reactive sputtering of germanium target in the atmosphere of a hydrocarbon: PVD - hydrogenated Ge:C (Ge:C:H) films [6]
- Plasma enhanced CVD (PE CVD) in the atmosphere of germane/hydrocarbon: CVD - hydrogenated Ge:C (Ge:C:H) films [7]
- Single source PE CVD in the atmosphere of an organogermanium compound: CVD - hydrogenated Ge:C (Ge:C:H) films [8, 9]

The present work is entirely devoted to the fourth method, i.e. to the deposition of hydrogenated Ge:C:H films using the single source PECVD technique. In particular, two tetraalkylgermanium compounds, and namely tetramethylgermanium and tetraethylgermanium, have been used in this work as starting materials.

EXPERIMENTAL

Reactor

A photograph presenting the parallel plate RF plasma deposition reactor is shown in Fig. 1. This reactor is supplied with the 13.56 MHz RF field from the Power Products RF5S generator using a customized matching network to minimize the reflected power.
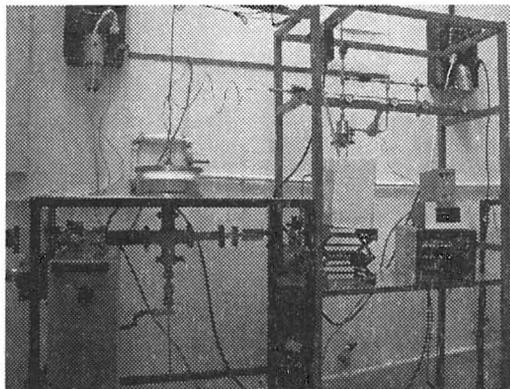
Fig. 1. A photograph of the parallel plate radio frequency plasma deposition reactor at work.

Starting materials

Two organogermanium compounds, whose structural formulae are presented in Fig. 2, were used as starting materials. Under normal conditions both these compounds are liquid. Therefore, they were both supplied to the system in a form of vapour carried by argon carrier gas. Tetramethylgermanium (Alfa product, b.p. 43.4°C, purity 99.5%) was used in 1-6% dilution in argon, while tetraethylgermanium (Alfa product, b.p. 165.5°C, purity 99.5%) was used in 1-3% dilution. The flow rate of a starting compound was controlled by means of controlling both the temperature of the liquid and the pressure above its surface.

GeMe₄
M=133

GeEt₄
M=189
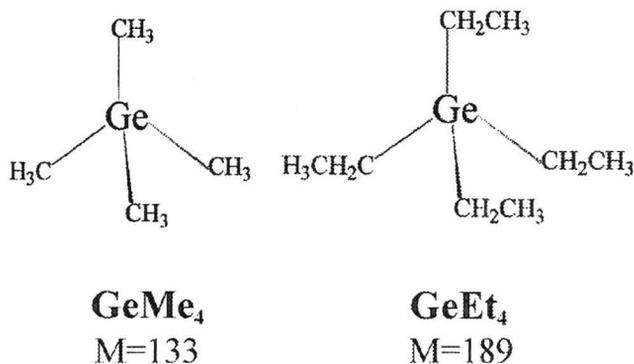
Fig. 2. Structural formulae of tetramethylgermanium and tetraethylgermanium.

Operational parameters

The principal operational parameters were: the flow rate of the organogermanium vapour, regulated in the range 0.1 – 0.6 sccm for tetramethylgermanium and in the range of 0.1 – 0.45 for tetraethylgermanium, and the RF power of discharge, regulated in the range of 2 – 110 Watt. System pressure was always kept at the 70 – 80 mTorr level. For the sake of comparisons, a combined operational parameter W/FM was often used in the processing of the results. In this parameter, W denotes the power input to the system, F denotes the flow rate of a starting material and M denotes its molecular weight. With the flow rate of organogermanium vapour expressed in mole/s units, the W/FM parameter is expressed in J/kg units and it gives an input of energy per unit mass of the starting material.

RESULTS

Deposition efficiency

Figure 3 presents dependencies of specific deposition yields for both starting compounds on the W/FM parameter. Although a clear separation of results corresponding to each compound is observed, in both cases the relationships consist of a mass excess range (where the yield increases with W/FM) and of an energy excess range (where the yield is independent of W/FM). It also apparent from the presented data that tetraethylgermanium exhibits a significantly higher tendency towards deposition than the tetramethyl derivative. This is very likely the effect of substantial differences in volatility (while saturated vapour pressure for tetramethylgermanium amounts to 426 Torr, it is only 2.66 Torr for tetraethyl-germanium) and, consequently, also in sticking coefficients of both compounds. Sticking coefficients of tetraethylgermanium, as well as of its major fragmentation products, must be much higher than those or tetramethylgermanium and its fragmentation products.
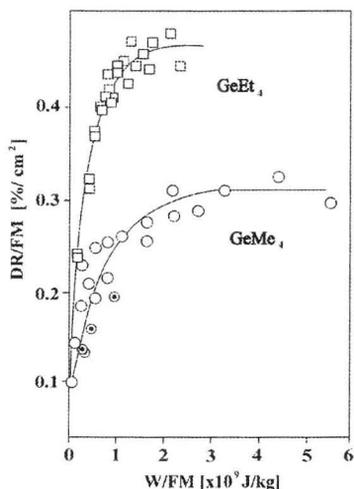
Fig. 3. Specific deposition yield for both precursor compounds vs. the W/FM parameter [9].
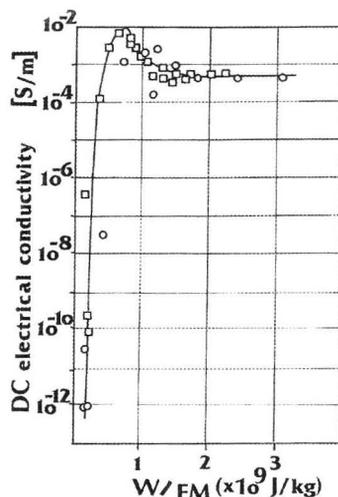
Fig. 4. DC electrical conductivity of films deposited from tetramethylgermanium (circles) and tetraethylgermanium (squares) as a function of the W/FM parameter [9].

Physical properties of the films

Films deposited at W/FM values below 0.6 GJ/kg are transparent and soft materials, forming polymer-like layers. Materials deposited at W/FM over 0.8 GJ/kg form, hard and black in colour films. In general, soft, polymer-like materials are characterized by densities below 2500 kg m^{-3} for methyl derivative and below 3000 kg m^{-3} for ethyl derivative.

DC conductivity

The results of DC conductivity measurements of films deposited from both starting compounds are presented in Fig. 4. All these results appear to follow the same pattern, consisting of three regions: an increasing dependence of conductivity on power parameter, characteristic for the softer films, a maximum and a saturation range, characteristic for the harder films. Both maximum and saturation conductivity values are in the range typical for plasma deposited thin amorphous semiconductor films.

Thermal activation plots of DC conductivity for three samples deposited from tetraethylgermanium are presented in Fig. 5. Thermal activation energy of DC conductivity, calculated from the above plots, amounts to approximately 0.3 eV for

sample A and to approximately 0.3 and 1.0 eV for both samples B and C. This magnitude of a thermal coefficient makes a given material an excellent candidate for the manufacture of thermistor devices.
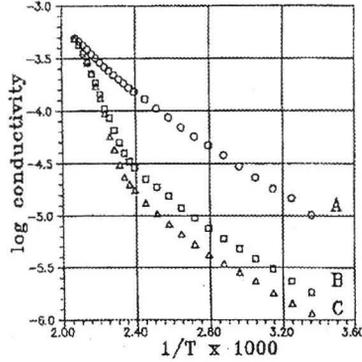
Fig. 5. Thermal activation plots of DC conductivity for three samples deposited from tetra-ethylgermanium [10]. A: W/FM = 0.8 GJ kg^{-1}, B: W/FM = 1.5 GJ kg^{-1} and C: W/FM = 2.0 GJ kg^{-1}.

Optical properties

Examples of spectral dependencies of refractive indices and extinction coefficients, recorded using variable angle spectroscopic ellipsometry (VASE), for soft and hard films deposited from tetramethylgermanium are presented in Fig. 6.

a)   b)
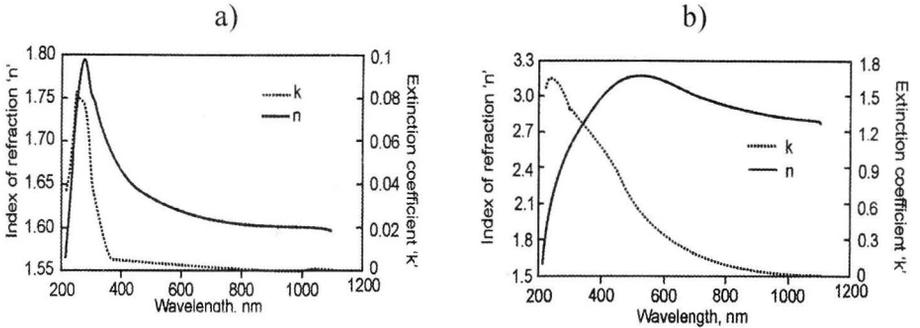
Fig. 6. Spectral dependencies of refractive indices and extinction coefficients for two samples deposited from tetramethylgermanium. a): W/FM = 0.17 GJ/kg and b): W/FM = 2.00 GJ kg^{-1}.

Optical gap

In the case of amorphous semiconductor materials, the width of the bandgap is often approximated with the so-called optical gap E_{opt}, defined by the Tauc law of an optical absorption for these materials [11]:

$$(\alpha \times E)^{1/2} = B^{1/2} \times (E - E_{opt}) \tag{1}$$

where α denotes the absorption coefficient, E denotes the energy of incident light quanta and B denotes a constant. Therefore, having in disposal light extinction data such as in Fig. 6, one can calculate the values of optical gap for the respective samples. These data have been collected for a large number of samples of films deposited from both starting compounds which gave rise to discuss the dependence of the film optical gap on the energetic parameters of its deposition, and namely on the W/FM parameter.

For both starting compounds optical gap values of materials deposited at W/FM values of 1.0 GJ kg^{-1} and above have been found to be independent of the W/FM parameter, amounting to 1.3 eV and to 2.2 eV for films manufactured from tetramethylgermanium and those deposited tetraethylgermanium, respectively. In both cases, however, deposition conditions resulting in the magnitudes of W/FM parameter lower than 1.0 GJ kg^{-1} produce materials whose optical gap values constitute a decreasing function of this parameter. The best illustration of this result is an instance of Ge:C:H films RF plasma deposited from tetramethylgermanium form which the magnitude of optical gap may be tuned in the range 1.3 – 3.2 eV, by means of applying the W/FM parameter in the range of 0.1 – 1.0 GJ kg^{-1} [12]. It is worth stressing that the above results are generally consistent with those of DC conductivity, presented in Fig. 4.

Chemical structure of the films

Two methods have been applied to determine chemical bonding in the discussed materials. One is the FTIR infrared absorption technique [13, 14] and the other is a high resolution solid state ^{13}C nuclear magnetic resonance method (^{13}C Cross Polarization Magic Angle Spinning NMR) [15]. While the former was used in order to determine all forms of bonding, the latter was applied specifically to record the proportions between sp^3 and sp^2 types of carbon hybridisation in the investigated materials.

FTIR spectra of a number of Ge:C:H films deposited from tetraethylgermanium at different W/FM parameters (B) are presented in Fig. 7, together with that of a starting compound itself (A). As seen in the figure the

spectra of films deposited at low energy loads to a large extent resemble the spectrum of tetraethylgermanium. This is a strong indication that the structure of these films is that of a loosely crosslinked organometallic polymer. It is an increasing magnitude of energy input that effects a change of the material structure from organometallic to an inorganic one.
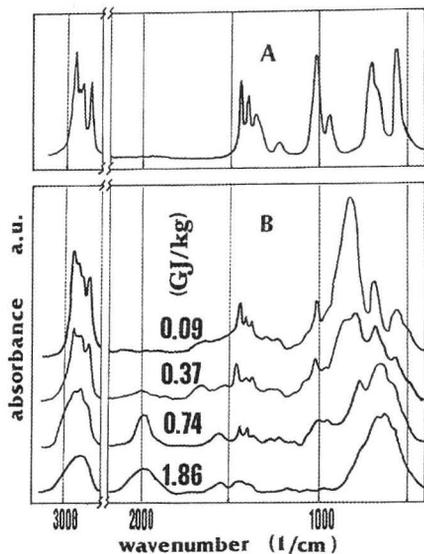
Fig. 7. Furrier transform infrared spectra of tetraethylgermanium (A) and of the films deposited from this starting compound under increasing W/FM parameter (B).
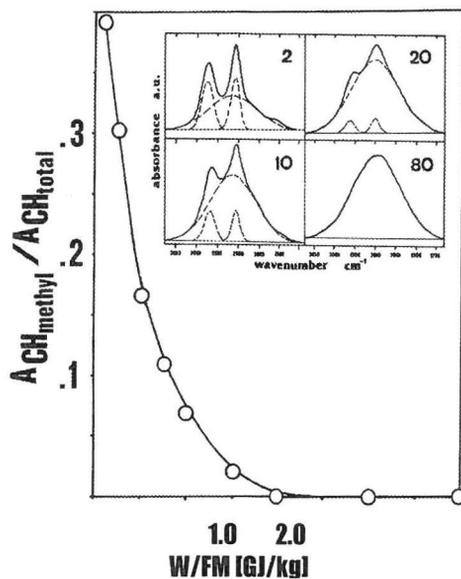
Fig. 8. A contribution of methyl group signals to the total area of C-H stretching band in films deposited from tetramethylgermanium as a function of W/FM parameter. Examples of curve fitting are given in the insert.

The character of this change is well illustrated in Fig. 8, with an example of C-H stretching absorption band (arising at approximately 3000 cm^{-1}) of films deposited from tetramethylgermanium at different W/FM values. For low W/FM values this band can be resolved into two sharp lines at ca. 2970 and 2900 cm-1, corresponding to asymmetric and symmetric vibrations of C-H bonds in methyl groups, and a broader signal centered close to the 2900 cm^{-1} line and corresponding to the vibrations of isolated C-H bonds in a stiff carbonous network. As seen in the figure, the contribution of methyl group signals to the total absorption connected with the C-H stretching vibrations drops dramatically with the W/FM parameter, reaching zero slightly above the value of W/FM = 1 GJ kg^{-1}.

The results of ^{13}C CP MAS NMR measurements for films deposited from tetraethylgermanium are presented in Figs 9 and 10. In Fig. 9, the 10-60 ppm range

is a sp^3 hybridisation range, while the 110-170 ppm range is that of sp^2 hybridisation. As seen, the sp^2 hybridisation is completely absent in the materials deposited at very low W/FM values and it only begins to appear between 0.5 and 1.0 GJ kg^{-1}. Figure 10 shows a correspondence of structural features recorded with FTIR and ^{13}C CP MAS NMR techniques, illustrating an evolution of a loose organometallic construction of the films to a dense inorganic structure.
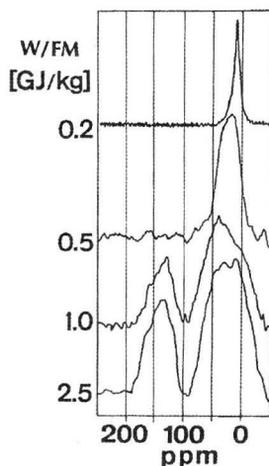
Fig. 9. ^{13}C CP MAS NMR spectra of films deposited from tetraethyl-germanium at different values of the W/FM parameter.
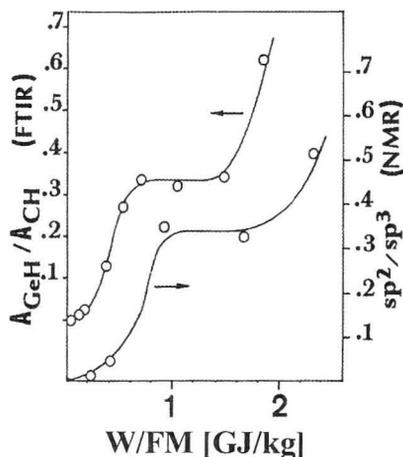
Fig. 10. Dependence of a ratio of integrated IR absorption of Ge-H to C-H stretching bands and a ratio of integrated NMR absorption of sp^2 to sp^3 hybridized carbon atoms on the W/FM parameter.

CONCLUSIONS

1. Parallel plate RF deposition of Ge/C films from tetraalkylgermanium derivatives results in materials of transport gap tunable within relatively broad range (1.3 – 3.2 eV for GeMe$_4$).

2. This technology is suitable for the manufacture of amorphous superlattice systems.

3. Thermal coefficients of DC conductivity make the films useful in thermistor technology.

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CIENKIE WARSTWY Ge:C:H WYTWARZANE Z PREKURSORÓW GERMANO-ORGANICZNYCH W PLAZMIE WYSOKIEJ CZĘSTOTLIWOŚCI

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S t r e s z c z e n i e. Przedstawiono plazmową metodę osadzania cienkich warstw Ge:C:H z tetrametyl- i tetraetylo-germanu w plazmie wysokiej częstotliwości. Warstwy osadzane przy wartości parametru W/FM poniżej 0.6 GJ/kg są przezroczyste, miękkie, o charakterze izolatorów i tworzą materiał polimeropodobny. Dla wartości W/FM powyżej 0.8 GJ/kg osadzany jest czarny, gęsty, twardy materiał półprzewodnikowy. Rezultaty badań strukturalnych wskazują na metaloorganiczny charakter otrzymanych polimeropodobnych warstw. Produkty mogą być wykorzystane w produkcji termistorów.

S ł o w a k l u c z o w e : cienkie warstwy, organiczne związki germanu, wyładowania wysokiej częstotliwości.