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Thin Films of Semiconductors and Dielectrics produced by Laser Evaporation

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Thin films of several III-V and II-VI compounds as well as of some dielectrics have been vacuum-deposited using a focused beam of a CO_2 or ruby laser to evaporate these materials. The crystallinity, morphology and the chemical composition of the produced thin films have been examined by various analytical methods. Films produced by the ruby laser were in most cases polycrystalline and stoichiometric, while films produced by the CO_2 laser were amorphous and non-stoichiometric. Different mechanisms of evaporation leading to the observed differences in characteristics of thin films are discussed.

1. Introduction

Preparation of thin films by vacuum evaporation is a familiar technique and has been applied to many materials with varying degrees of success. Several serious drawbacks make this technique unsuitable in some cases, e.g. attempts to prepare thin films of incongruently evaporating compounds result in films containing an excess of the more volatile component. Furthermore, conventional evaporators contain various heating elements, such as evaporant heaters, substrate heaters etc with which the evaporating substance and the film come into contact and possibly react thus introducing undesirable impurities in the resulting films.

A technique designed to circumvent the problem of incongruent evaporation is "flash evaporation" [1] in which a small amount of a material is rapidly and completely evaporated, thus yielding films of the same composition as the evaporant. Another technique is that of "co-evaporation" [2], where substances are evaporated at different rates and then brought into contact at the substrate where the reaction results in a film of the desired composition. However, the problems of the evaporant-evaporator interaction, and thus impurity problems, have not been solved by the improvements mentioned above, and these methods have produced satisfactory films of only a limited number of materials.

As a next step, methods have been designed in which only a selected portion of evaporant is heated. Among these, electron beam heating and ion bombardment (sputtering) are most often used, and a wide variety of films have been prepared in this way. However, these methods lead to some new problems, the most important being rather low deposition rates and the requirement of complicated and expensive experimental set-ups.

Recently, the use of the laser beam to evaporate materials in order to deposit thin films has been suggested. So far, a rather limited number of publications describe efforts in this direction: Smith and Turner [3], Nichols [4], Zavitsanos and Sauer [5], and Schwarz and Tourtellotte [6] used pulsed ruby or neodymium-doped glass lasers. Groh [7] and Hass and Ramsay [8] have used continuous-wave CO_2 lasers. The results of the experiments mentioned above vary from material to material, but they demonstrate the feasibility of this method. In addition, recent studies of laser-induced evaporation of solids [9-11] revealed certain aspects of the laser-solid interaction which could be exploited in the preparation of thin films; this will be discussed in more detail later.

Laser evaporation offers several important advantages over the other evaporation methods, e.g.

(*a*) the laser is mounted outside the vacuum chamber and only a small selected area of the evaporant is heated and evaporated by the laser beam, thus excluding undesirable interactions; this can result in extremely pure films;

(*b*) since the rest of the system is not heated, one can introduce a variety of gases into the evaporat-

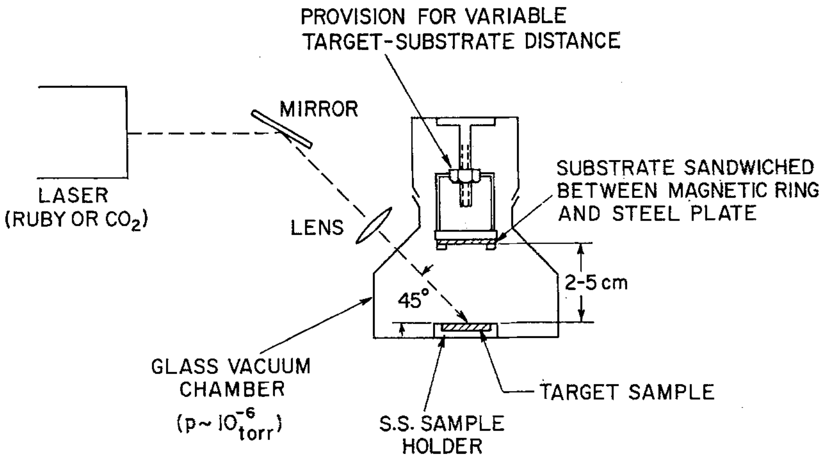

Figure 1 Schematic representation of apparatus used in laser evaporation experiments.

ing chamber and thus achieve effects similar to "reacting sputtering"; this can be utilised in doping the produced films;

(*c*) film deposition rates of more than 1000 Å/min are readily achievable with present-day lasers;

(*d*) it has been shown that laser evaporation results in the congruent evaporation of some materials which normally evaporate incongruently, e.g. III-V compounds, when evaporated by a laser beam, yield films of the same composition (this effect will be discussed later);

(*e*) it has been determined that crystalline films have been obtained in some cases despite the fact that deposition occurred on substrates kept at room temperature.

For these reasons, we decided to examine the use of lasers for the preparation of thin films of several electronically important materials, which are usually difficult to produce by any other method. In this report we shall describe the results of our attempts to prepare laser-deposited thin films of:

(i) III-V compounds, e.g. GaP, GaAs, GaSb, InAs;

(ii) II-VI compounds, e.g. ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe;

(iii) various dielectrics, e.g. Al_2O_3, SiO_2, $CaTiO_3$, $MgAl_2O_4$, $CdCrS_4$, $CdCrSe_4$.

In particular, we are interested in stoichiometry, morphology and crystallinity of the obtained films.

2. Experimental

In most of our experiments a pulsed ruby laser operating in a non-Q-switched mode was used. It is capable of delivering 2.2 J output energy in a 500 μsec pulse. The power density of the focused laser beam is estimated to be between 10^7 and 10^8 W/cm^2.

A continuous wave CO_2 laser was used in some cases; it produced a power output between 10 and 50 W. In this case, the power density of the focused beam was about 10^5 W/cm^2. A special optics, transparent to the 10.6 μm radiation, was used in connection with the CO_2 laser.

A schematic representation of the vacuum ($\sim 10^{-6}$ torr) evaporation chamber is given in fig. 1. Loosely packed powder, or in some cases, pelletised powder was placed in a stainless steel cup. The focused laser beam entering the chamber through an optically flat window (glass in the case of the ruby laser, NaCl in the case of the CO_2 laser) was incident upon the target surface at a 45° angle. The beam was focused by a lens with a focal length of 5 cm (a Ge lens was used in the case of the CO_2 laser). Thin films were deposited on substrates placed 2 to 5 cm directly above the evaporating target and kept at room temperature. Microscope slides or carbon-coated copper meshes (in order to facilitate subsequent electron microscope experiments) were used as substrates. Films were deposited over an area of approximately 1 cm^2.

From the weight gain of the substrates and from the quantitative chemical analysis of the deposited material we estimate that for most substances films of about 50 ± 25Å were deposited with each pulse of the ruby laser. Since our laser had a low pulse repetition rate (1 pulse/120 sec), films thicker than 2000 to 3000 Å could not be deposited within a reasonable length of

TABLE I Thin films produced by CO_2 laser evaporation of solids

Material	Rate of deposition Å/sec	Composition of thin film	Quality of thin film	Remarks
GaP	100 to 300	Ga_xP_{1-x} $x = 0.02$ to 0.05	amorphous, uniform free of inclusions	incongruent evaporation
GaAs	100 to 300	Ga_xAs_{1-x} $x = 0.02$ to 0.1	amorphous, uniform free of inclusions	incongruent evaporation
GaSb	100 to 300	$GaSb_{1-x}$ $x = 0.02$ to 0.1	amorphous, uniform free of inclusions	incongruent evaporation
$CaTiO_3$	undetectable	---	---	very difficult to evaporate
$MgAl_2O^4$	undetectable	---	---	very difficult to evaporate

TABLE II Thin films produced by ruby laser evaporation of solids

Material	Composition of thin film	Quality of thin film	Remarks
III-V Compounds			
GaP	GaP	uniform, polycrystalline	
GaAs	GaAs	uniform, polycrystalline	
GaSb	GaSb	uniform, polycrystalline	
InAs	InAs	uniform, polycrystalline	
II-VI Compounds			
ZnO	uncertain, probably ZnO and Zn	uniform, very poor crystallinity	impossible identification due to diffuse diffraction rings
ZnS	ZnS	uniform, polycrystalline	
ZnSe	ZnSe	uniform, polycrystalline	
ZnTe	ZnTe	uniform, polycrystalline	
CdS	CdS	uniform, polycrystalline	
CdSe	CdSe	uniform, polycrystalline	
CdTe	CdTe	uniform, polycrystalline	
Dielectrics			
Al_2O_3	uncertain, probably Al_2O_3	uniform, very poor crystallinity	very diffuse diffraction pattern
SiO_2	uncertain, probably SiO_2	uniform, very poor crystallinity	very diffuse diffraction pattern
$CaTiO_3$	$CaTiO_3$	uniform, very good crystallinity	some inclusions due to splashing
$MgAl_2O_4$	uncertain	uniform, amorphous	poor diffraction pattern
$CdCr_2S_4$	uncertain	uniform, amorphous	poor diffraction pattern
$CdCr_2Se_4$	uncertain	uniform, amorphous	poor diffraction pattern

time. In experiments with the CO_2 laser, deposition rates of 150 to 300 Å/sec were achieved.

All films were characterised by transmission electron diffraction. The characteristic diffraction rings yielded information on the crystallinity as well as on the number of phases present on the film, thus confirming or disputing the congruency of evaporation. The composition of several films was also examined by other methods, such as electron microprobe and wet chemical analysis. The morphology of various films was examined by optical microscopy, transmission electron microscopy and by scanning electron microscopy.

3. Results

3.1. CO_2 Laser

Several substances have been evaporated by the focused continuous beam of the CO_2 laser. The results of these experiments are summarised in table I.

The results in the case of III-V compounds remind us of the attempts to prepare these materials by methods of conventional evaporation. The resulting films contain a large excess of the more volatile component.

Attempts to evaporate $CaTiO_3$ and $MgAl_2O_4$ were unsuccessful. This is consistent with reports in [7] and [8] where compounds of similar type have been evaporated only with difficulties, or not at all in some cases.

3.2. Ruby Laser

Thin films produced by ruby laser evaporation are listed in table II. For the III-V and the II-VI compounds (except for ZnO), the results of the diffraction analysis indicate that congruent evaporation took place and the resulting films have the same composition as the target material.

The chemical composition of some films was also examined by the electron microprobe and by the wet chemical analysis. Due to the thinness of films, the uncertainty of the results obtained was of the order of a few at. %. No consistent deviations from stoichiometry were observed in the analysed films. Mass spectrometric analysis of laser-produced vapours of III-V compounds demonstrated that the evaporation rates of both elements are of the same order of magnitude [11].

In the case of dielectrics, results varied from the very good crystalline film of $CaTiO_3$ (consistent with reference [6]), to poorly defined films of $MgAl_2O_4$ and other spinels ($CdCr_2S_4$ and $CdCr_2Se_4$), where the observed diffraction rings were diffuse and an unambiguous assignment of composition was not possible.

The morphological examination by means of various microscopic techniques showed that certain amounts of splashed melt particles were imbedded in the deposited films. The splashing effect as well as the possible ways of reducing it are discussed in reference [6].

The transmission electron micrograph showed that in the initial stages of deposition small coalescing crystallites are formed (fig. 2). In the case of InAs, the size of these crystallites was found to be 250 ± 50 Å. Further deposition results in continuous polycrystalline films. This was confirmed by the results of the scanning electron microscopy.

4. Discussion

The results of our experiments indicate that successful deposition of thin films of various materials is possible by means of the laser evaporation technique. However, significant differences in the results of the CO_2 laser evaporation and the results of the ruby laser evaporation have been observed; these will be discussed in this section.

The main differences are:

(*a*) the incongruent evaporation of the III-V compounds by means of the CO_2 laser versus the congruent evaporation of these materials resulting from the ruby laser experiments; and

(*b*) the ability of the ruby laser to evaporate several refractory materials.

The ruby and the CO_2 lasers differ in the wavelength of the emitted beam, in the power density delivered (10^8 W/cm^2 and 10^5 W/cm^2, respectively) as well as in the mode of operation (pulsed and continuous, respectively). The last two factors lead to different regimes of evaporation resulting from the laser-solid interaction.

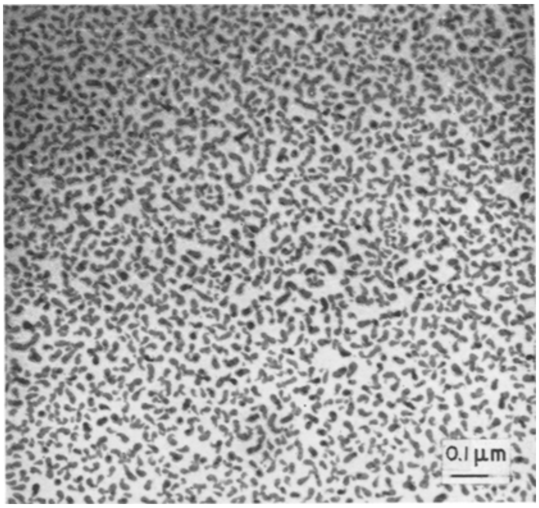

Figure 2 Transmission electron micrograph of an InAs film in the early stage of growth.

We shall briefly review the discussion of the mechanism of ruby laser-solid interaction, presented by one of us elsewhere [12, 13].

Surface temperatures as high as 4000 to 9000° K are usually achieved in the interaction of a 10^8 W/cm^2 beam with solids [14, 15]. These temperatures are reached in about 10^{-7} sec. The resultant vapour escaping throughout the duration of the laser pulse forms a rapidly expanding jet. This jet moves with a velocity of about 10^5 cm sec [16] and exerts a recoil pressure on the condensed phase as high as 10^3 to 10^4 atmospheres [17, 18] (critical temperatures and pressures for most inorganic materials are similar to, or smaller than, those accompanying the laser-solid interaction). At the critical point, the heat of vaporisation of all substances drops to zero and the complete evaporation leading to stoichiometric films takes place.

In the case of the CO_2 laser, a beam of much lower power density interacts with the target, and the resulting temperatures and pressures are correspondingly lower. Thus, evaporation occurs under conditions similar to conventional evaporation, and the films obtained are also similar, i.e. non-stoichiometric.

Since CO_2 laser evaporation typically lasted from 30 to 150 sec, significant heating of the area surrounding the beam impact point could take place, thus leading to further evaporation of the more volatile component.

In the case of the ruby laser, very steep thermal gradients (10^6 deg/cm) as well as the fast temperature change rates (10^{10} deg/sec) occur [19], thus leading to complete evaporation of a relatively small volume, without seriously affecting the rest of the sample.

The craters formed in our experiments are about 500 to 1000 μm in diameter and in depth. A significant fraction of this volume evaporates within 500 μsec, thus leading to the observed high deposition rates.

Although this complete evaporation of a small volume is reminiscent of the flash evaporation technique, our previous experiments [10] demonstrated significant differences between the laser- and flash-evaporation processes and we feel that the mechanism described above is more probable than the simple flash evaporation.

5. Conclusions

From the results of our experiments one might conclude that:

(*a*) pulsed lasers can deposit thin films of many interesting materials at useful deposition rates;

(*b*) stoichiometric deposition resulting from the ruby laser-solid interaction could be utilised in the preparation of thin films of materials which normally evaporate incongruently;

(*c*) results obtained with the CO_2 laser are reminiscent of results obtained in conventional evaporation experiments.

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References

1. L. HARRIS and B. M. SIEGEL, *J. Appl. Phys.* **19** (1948) 739.
2. K. G. GUNTHER, *Z. Naturforsch* **13** (1958) 1081.
3. H. M. SMITH and A. F. TURNER, *Appl. Opt.* **4** (1965) 147.
4. K. G. NICHOLS, *Brit. Commun. Electron* **12** (1965) 368.
5. P. D. ZAVITSANOS and W. E. SAUER, *J. Electrochem. Soc.* **115** (1968) 109.
6. H. SCHWARZ and H. A. TOURTELLOTTE, *J. Vac. Sci. Technol.* 6 (1969) 373.
7. G. GROH, *J. Appl. Phys.* **39** (1968) 5804.
8. G. HASS and J. B. RAMSAY, *Appl. Opt.* **8** (1969) 1115.
9. B. E. KNOX, V. S. BAN, and J. SCHOTTMILLER, *Mat. Res. Bull.* **3** (1968) 337.
10. B. E. KNOX and V. S. BAN, *Mat. Res. Bull.* **3** (1968) 885.
11. V. S. BAN and B. E. KNOX, *Internat. J. Mass Spectròm Ion Phys.* **3** (1969) 131.
12. *Idem, J. Chem. Phys.* **51** (1969) 524.
13. *Idem, ibid* **52** (1970) 243.
14. R. E. HONIG, *Appl. Phys. Letters* **3** (1963) 8.
15. V. P. VEIKO, YA. A. IMAS, A. N. KOKORA, and M. N. LIBENSON, *Sov. Phys. —Tech. Phys.* **12** (1968) 1410.
16. J. A. HOWE, and T. V. MOLLOY, *J. Appl. Phys.* **35** (1964) 2265.
17. G. A. ASKAR'YAN and E. M. MOROZ, *Sov. Phys.— JETP* **16** (1963) 1638.
18. R. M. WANIEK and P. J. JARMUZ, *Appl. Phys. Letters* **12** (1968) 52.
19. J. F. READY, *J. Appl. Phys.* **36** (1965) 462.

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