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HYDROGENATED AMORPHOUS SILICON PRODUCED BY LASER INDUCED CHEMICAL VAPOR DEPOSITION OF SILANE

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a-Si:H films deposited by laser induced CVD (LICVD) have been charaterized and the growth process modelled. Growth rates are exponentially dependent on gas temperature and film properties follow the equilibrium hydrogen content, exponentially dependent on substrate temperature.

INTRODUCTION

Structurally superior a-Si:H films are produced by chemical vapor deposition (CVD) from silane,[1] but they contain insufficient hydrogen to achieve good electronic properties because high substrate temperatures (T_s = 600°C) are necessary for reasonable deposition rates. In the laser-induced CVD (LICVD) process,[2,3,4] sketched in Fig. 1, a CO_2 laser beam [P(20) line: 10.591 μm] impinges on a gas mixture parallel to the substrate upon which the film is deposited. The reactant gases, which include SiH_4, are heated directly by absorbing infrared photons, allowing precise, and independent control of both the gas temperature, T_g, and the substrate temperature, T_s. This provides a major advantage of the technique; high deposition rates can be achieved at low substrate temperatures. Since the defect structure is predominantly determined by T_s, we anticipated that LICVD films would exhibit excellent properties.

GROWTH MODEL

Deposition of a-Si:H films by LICVD requires the gas-phase reaction, $SiH_4(g) \rightarrow SiH_2(g) + H_2(g)$, which takes place at temperature T_g; diffusion of the SiH_2 free radicals towards the substrate; and film growth via a combination of deactivation and hydrogen elimination, processes which take place at temperature T_s.[4] The rate-limiting step is probably the SiH_4 dissociation reaction causing the growth rate $G(T_g)$ to be exponentially dependent on T_g. We calculated steady-state T_g's by equating the absorbed laser energy with the heat lost by thermal conduction.[5] This predicts an increase of T_g with increasing laser power, silane partial pressure, and T_s and with decreasing thermal conductivity of the gas mixture. For example, using pure SiH_4 at pressures of 5 torr (with T_s = 400°C) to 8 torr (with T_s = 200°C), laser power of 20-40 W, we calculate T_g's between 440-550°C. An Arrhenius plot of $G(T_g)$ is linear in the region over

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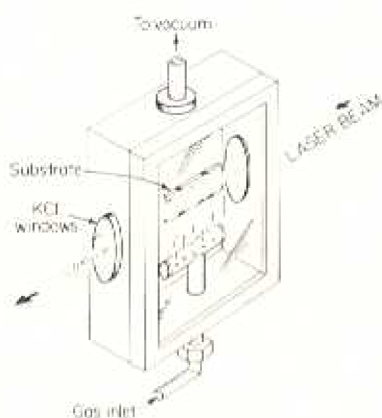

Fig 1. Schematic diagram of the LICVD Reactor.

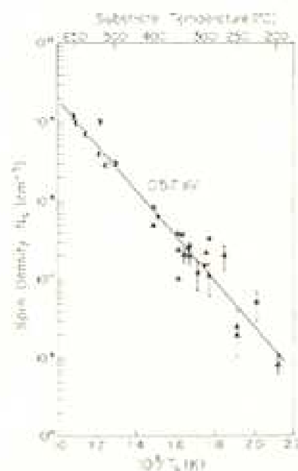

Fig 2. Spin density, N_s, vs $1/T_s (K^{-1})$ for LICVD films, ●25W, ▲40W, ▼45W laser powers above the sub-strate, and for normal CVD films ◐, ◐.[8]

which our estimate of T_g is expected to be accurate,[4] yielding an activation energy of 46 kcal/mol, essentially the same as observed for the pyrolysis of SiH_4.[6] This is consistent with our identification of this as the rate-limiting step in film growth.

The LICVD technique has some similarities to the HOMOCVD process,[7] in that both proceed after a homogeneous thermal decomposition of SiH_4. However, due to the high degree of spatial control possible with the laser LICVD is subject neither to parasitic reactions near the hot walls nor to contamination from heated surfaces.

FILM PROPERTIES

Adherent films have been deposited on borosilicate glass, fused silica, aluminum, and single-crystal silicon substrates. All films were determined to be amorphous by TEM.

Electron spin resonance (ESR) measurements indicated the existence of neutral dangling-bonds (g = 2.0055). The unpaired-spin concentration, N_s, is a sensitive function of T_s only. Fig. 2 shows an Arrhenius plot of N_s versus T_s for both LICVD and conventional CVD a-Si:H films.[8] All the data are fit by the relationship, $N_s = (1.5 \times 10^{22} cm^{-3}) \exp(-0.57\ eV/kT_s)$ emphasizing the basic

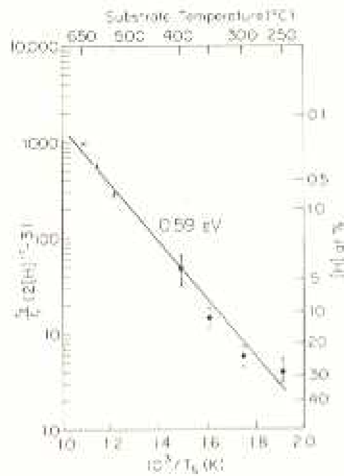

Fig 3. Hydrogen content and $r_2/r_1 = 2[H]^{-1}-3$ vs 1/T for LICVD films and for CVD(+)[11].

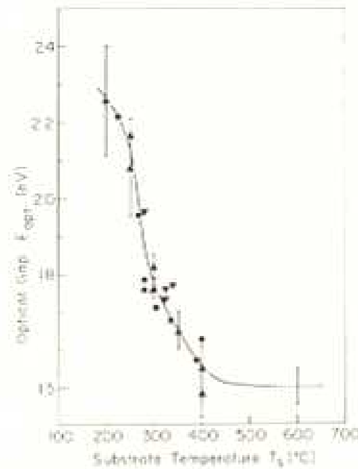

Fig 4. Optical gap, E_{opt}, vs T_s (°C) for LICVD films and for normal CVD films (+).[12]

similarities of the two processes. However, the LICVD process permits films to be deposited at T_s values that are inaccessable to conventional CVD. The N_s values, > 8 x 10^{15} cm^{-3}, equal other high-quality films and importantly do not exhibit the minimum in N_s observed near T_s = 300°C for glow-discharge[9] or HOMOCVD[7] deposited a-Si:H. These LICVD results show that an equilibrium number of dangling bonds form during growth at T_s with a formation energy of 0.57 eV.

The hydrogen concentration, [H], was determined by the effusion technique.[9] Kampas and Griffith[10] proposed a model for the growth of a-Si:H films which relates the ratio of the rates of deactivation, r_1, and hydrogen elimination, r_2, to the function, $2[H]^{-1}-3$. An Arrhenius plot of this function versus T_s is shown in Fig. 3 for both LICVD films and conventional CVD films;[11] the plot is linear with an activation energy of 0.59 eV for r_2/r_1. This value, essentially the same as for dangling bond creation, represents the difference in activation energies of the deactivation and H-elimination processes.

The optical gap, E_{opt}, of our films, obtained from Tauc plots, is shown as a function of T_s in Fig. 4. E_{opt} is independent of laser power, but decreases sharply with increasing T_s in the 200-400°C range, because of the sharp decrease in [H] over this range.

CONCLUSIONS

We have shown that LICVD a-Si:H films are superior to those produced by conventional CVD. The best LICVD films had $N_s = 8 \times 10^{15} cm^{-3}$ and were deposited at the lowest T_s (= 200°C) investigated. At this T_s, E_{opt} = 2.3 eV and [H] = 30 at %. The film growth rate appears to be controlled by the thermal decomposition of SiH_4 at T_g, while the dangling bonds appear to be created at T_s with a formation energy of 0.57 eV. The separate control of T_g and T_s, possible with LICVD, permits high-quality films to be produced at reasonable deposition rates.

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REFERENCES

1. M. Hirose, J. de Physique, C4 (1981) 705-14.

2. T. R. Gattuso, M. Meunier, D. Adler and J. S. Haggerty, Materials Research Society Symposia Proceedings, Laser Diagnostics and Photochemical Processing for Semiconductor Devices, 17 (1983) 215-22.

3. M. Meunier, T. R. Gattuso, D. Adler and J. S. Haggerty, Appl. Phys. Lett., in press.

4. M. Meunier, J. H. Flint, D. Adler and J. S. Haggerty, J. Elec. Mat., in press.

5. M. Meunier, J. H. Flint, D. Adler and J. S. Haggerty, to be published.

6. C. G. Newman, H. E. O'Neal, M. A. Ring, F. Leska and N. Shipley, Int. J. Chem. Kinetics, XI (1979) 1167.

7. B. A. Scott, J. A. Reimer, R. M. Plecenik, E. E. Simonyi and W. Reute, Appl. Phys. Lett. 40 (1982) 973; B. A. Scott, R. M. Plecenik and E. E. Simonyi, Appl. Phys. Lett., 39 (1981) 73.

8. S. Hasegawa, T. Kasajima and T. Shimizu, Phil. Mag. B, 43 (1981) 149-56; P. Hey and B. O. Seraphin, Sol. En. Mat., 8 (1982) 215-30.

9. H. Fritzsche, Sol. En. Mat., 3 (1980) 447-501.

10. F. J. Kampas and R. W. Griffith, Appl. Phys. Lett. 39 (1981) 407.

11. P. C. Booth, D. D. Allred and B. O. Seraphin, J. Non-Cryst. Solids, 35-36 (1980) 213.

12. M. Janai and B. Karlsson, Sol. En. Mat., 1 (1979) 387-95.