PHOTON-CONTROLLED GROWTH OF MULTILAYERED STRUCTURES

DOUGLAS H. LOWNDES, D. B. GEOHEGAN, D. ERES, D. N. MASHBURN and S. J. PENNYCOOK; Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6056

ABSTRACT

Pulsed ArF excimer laser (193 nm) photolysis has been used to deposit entirely amorphous and mixed amorphous/polycrystalline superlattice structures containing Si, Ge and Si_3N_4. High resolution in situ optical reflectivity measurements were used to monitor and/or control deposition. Transmission electron microscope cross-section views demonstrate that amorphous superlattice structures having highly reproducible layer thicknesses (from about 50 to several hundred Å), and sharp interlayer boundaries, can be deposited at low substrate temperatures under laser photolytic control.

INTRODUCTION

The growing number of applications for structures composed of alternating thin layers of crystalline or amorphous materials has given new impetus to the search for alternative low temperature thin film deposition techniques. For semiconductors, low temperatures are needed when multilayered structures contain highly doped adjacent layers, in order to avoid dopant interdiffusion during growth. For semiconductors and other materials, low deposition temperatures minimize in-diffusion of unwanted impurities from the surroundings, prevent interdiffusion with the substrate or other adjacent materials, and provide unique access to any low temperature phases that may exist. However, conventional thermally driven (pyrolytic) chemical vapor deposition (CVD) film growth reactions usually are limited to very low, or even negligible, film growth rates at low temperatures.

In this paper we describe an alternative to pyrolytic growth, namely, direct photolysis of precursor gas molecules, using pulsed ArF (193 nm) excimer laser radiation. The principal advantage of pulsed-laser photolysis for fabrication of amorphous multilayered structures is that high resolution can be obtained in layer thickness, because deposition is inherently "digital": Each laser pulse produces much less than a monolayer of film, on average. Nevertheless, the high pulse repetition rate of excimer lasers permits high deposition rates to be achieved at low temperatures. We also describe an optical reflectivity technique that provides sub-monolayer resolution film thickness monitoring. The combination of high resolution optical monitoring with pulsed laser photolysis can, in principle, provide monolayer accuracy in controlling the average thickness of deposited layers. We report results of experiments in which we have explored deposition of superlattice structures containing amorphous semiconductor and dielectric thin film layers, using these techniques.

EXPERIMENTAL CONDITIONS

Multilayer growth experiments were carried out in a deposition chamber [1] based on a six-way stainless steel cross and equipped with 2-in.-diam Suprasil windows. All depositions were made onto 2.5-cm square (100) crystalline (c) Si substrates; the substrate temperature was measured with an infrared radiation thermometer (IRCON Type W). The ArF laser beam (15 ns

Mat. Res. Soc. Symp. Proc. Vol. 103. ©1988 Materials Research Society

FWHM pulse duration) was unfocused and parallel to the substrate; it was passed through a rectangular slit before entering the chamber, to more precisely define its cross section (6 x 20 mm^2), and the bottom edge of the beam was set 1 mm above the substrate's surface.

Amorphous (a) Si was deposited by photolysis of disilane (Si_2H_6), Si_3N_4 by photolysis of a mixture of disilane and ammonia (NH_3), and a-Ge by photolysis of germane (GeH_4). In addition to these gases, He was used to flush the inside of the two windows through which the excimer laser beam entered and exited the deposition chamber. He flow conditions were found [1] that would nearly completely eliminate the rapid deposition of Si or Si_3N_4 films, which will otherwise occur on these windows, resulting in a rapid decrease of laser power and preventing accurate monitoring of the laser power within the chamber. The He flush did not prevent a very gradual decay of laser power due to Ge film deposition on the windows. However, we found that the Ge film buildup is a strong function of the incident laser intensity; by operating at low fluence during the a-Ge depositions it was possible to forestall Ge window-film buildup.

Because the absorption cross-section of germane is very small [2] at 193 nm, our a-Si/a-Ge multilayers were fabricated in two different ways. Structures containing relatively thin (<100 Å) a-Ge layers were grown entirely by photolysis, but thicker a-Ge layers were grown by pyrolysis, in order to obtain reasonable growth times and to minimize the gradual loss of laser power due to Ge film deposition on the windows. However, pyrolytic growth of a-Ge required working at a higher substrate temperature of 390°C. The completely photolytic a-Ge/a-Si structure was deposited at 250°C. Its a-Si layers used 40 sccm of a 10% disilane/90% He mix at p=5 Torr, 40 Hz laser rep rate and 200 mW of transmitted laser power. The a-Ge layers were deposited using 140 sccm of a 10% germane/90% He mix at p=50 Torr, 60 Hz rep rate and 420 mW transmitted power. A He window purge of 450 sccm (total) was used continuously. The only major differences for the structure with pyrolytically grown a-Ge layers were that the flow rate of germane mix was 20 sccm with p=5 Torr and no window flush, and the carrier gas for both silane and germane was H_2 rather than He. In this case, we observed a long "incubation time" (5–10 min) before pyrolytic growth of each a-Ge layer could begin. We speculate that this may have been due to H_2 covering the previous a-Si layer and preventing nucleation of a-Ge. We also found that photolytic deposition of a-Ge from GeH_4/H_2 mixtures was much slower than from GeH_4/He.

Several a-Si/Si_3N_4 multilayers were grown at 350°C and p=5 Torr. For the a-Si layers, a 10% disilane/90% H_2 mixture was used at a flow of 20 sccm; for the SiN_3N_4 layers 60 sccm of NH_3 and 20 sccm of the disilane mix were used (~30:1 NH_3:Si_2H_6 ratio). At 350°C, measurements that are reported elsewhere [1] show that the ratio of our photolytic and "background" pyrolytic deposition rates for a-Si is about 1000:1, so that film deposition is completely photonically controlled.

Monitoring and Control of Multilayer Growth

We have developed an optical reflectivity technique for rapidly and precisely measuring film deposition rates under varying conditions [1]. A low-power HeNe (632.8 nm) laser beam is reflected from the gas-film and film-substrate interfaces at near-normal incidence and the reflected beam is detected using a large-area Si photodiode. Using this techique, it is possible to monitor film deposition in real time with a resolution of ~0.002Å (where the film thickness is averaged over the HeNe laser's ~0.5 mm diam unfocused spot size). Thus, submonolayer resolution easily is obtained and deposition rates <0.001 Å/min can be measured [1].

Figure 1 shows the reflectivity signal obtained during deposition of an a-Si film by photolysis of disilane. This figure illustrates that essentially complete "photonic" control of deposition can be obtained:

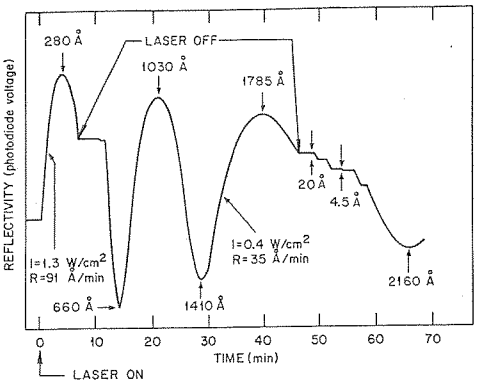

Fig. 1. Photo-controlled deposition of a-Si on an oxidized c-Si substrate. (ArF laser: 40 Hz and 1 W/cm^2; 10% disilane/90% He at 20 sccm; 5 Torr, 350°C.)

Deposition ceases when the laser is turned off, and film thickness steps of only a few Angstroms are introduced easily. In fact, the mean deposition rate of ~1 Å/sec in this experiment was obtained at a laser pulse repetition rate of 40 Hz, so that each laser pulse corresponds to deposition of only a very small fraction (~0.02 Å) of a monolayer (averaged over the HeNe beam spot). The substrate temperature is sufficiently low that the "background" thermal growth rate is negligible [1]. Thus, direct "photonic" control appears to be a feasible method for fabricating amorphous superlattice structures.

The results shown in Fig. 1 suggest two methods for controlling the growth of multilayered and superlattice structures: (1) "open loop" control, in which the average laser power transmitted into the chamber and the number of laser pulses are monitored, with corresponding layers deposited such that the product of (power)×(no. of pulses) is kept constant; (2) "closed loop" control, in which the actual film thickness is monitored and used to determine the end point for each layer. Open loop control assumes that the deposition rate for each material can be calibrated in advance. It then depends upon accurate measurement of the laser power and upon non-laser-related parameters, such as gas flows and pressure, remaining constant during deposition. The practical limit for this case is set by the stability and reproducibility of power meters, mass flow controllers, pressure controllers, etc., and by the accuracy with which the UV laser power in the chamber can be measured. Closed loop ("feedback") control places less stringent requirements on controllers and meters, but requires continuous, accurate in situ monitoring of the actual film thickness. For this to be possible, it is necessary to calculate the reflectivity signal that will be obtained during deposition of a multilayered structure, i.e., the optical constants of the various layers must be known under the actual deposition conditions. In addition, it must be assumed that interlayer interactions (diffusion, chemical reactions, phase transformations) either do not occur during growth or occur in ways that can be modeled. Considering the latter constraint, deposition at low substrate temperatures has obvious advantages.

Laser Photochemical Vapor Deposition (LPVD) Reactions

Although deposition from disilane, germane and ammonia mixtures has been studied under a variety of conditions, no definitive studies of the reaction chemistry leading to deposition have been presented in the literature. Deposition of Ge by photolysis of GeH_4 relies upon a very small ($< 4 \times 10^{-19}$ cm^2) absorption cross section at 193 nm [2]. Nevertheless, at temperatures < 275°C and high pressures (~200 Torr), photolytic deposition at modest laser fluences (15 mJ/cm^2) dominates the pyrolytic deposition rate [3]. While germylene (GeH_2) is probably produced at the surface by pyrolysis of germane, growth of the hydrogenated germanium film may involve a series of insertion reactions involving GeH_2 followed by desorption of H_2 [4]. In addition to GeH_2, the photolytic reaction may produce other intermediates such as GeH, GeH_3, Ge_2H_6 and atomic Ge [3].

Amorphous Si deposition from disilane by pyrolysis and by 193 nm photolysis is discussed in detail in another paper [1]. The absorption cross section at 193 nm ($\sim 3 \times 10^{-18}$ cm^2) is significantly larger than for GeH_4 [2]. The primary products of photodecomposition of Si_2H_6 are thought to be SiH_3SiH and H_2 while secondary gas-phase reactions produce such intermediates as SiH, SiH_3 and Si_2H_6, which have for their final product $(SiH_2)_n$ deposits on the surface. Above 200°C, H_2 desorbs from the surface, leaving silicon. Thermal growth of silicon involves the decomposition of Si_2H_6 into SiH_4 and SiH_2, followed by a complicated series of silylene insertion reactions yielding $(SiH_2)_n$ deposits, as in the photolytic case.

The reaction chemistry leading to growth of Si_3N_4 by photolysis of ammonia and silane (or disilane) mixtures is even more complex and has not yet been determined. Under irradiation at 193 nm, NH_3 is strongly absorbing ($\sigma_{193} = 1.7 \times 10^{-17}$ cm^2) [6] and photodissociates predominately to NH_2 (X $^2B_1$) + H with only a small percentage (2.5%) going to NH_2 (A $^2A_1$). The excited NH_2 (A $^2A_1$) state can absorb another photon, dissociating to NH (A $^3\Pi$) + H but this is energetically impossible for the majority of dissociated NH_2 in the (X $^2B_1$) state [5]. Considering the variety of intermediates formed during photolysis of Si_2H_6, the chemistry becomes quite complicated. In work with mercury-photosensitized reactions of SiH_4/NH_3 mixtures, however, Wu identified several Si-N-containing intermediates including silylamine (SiH_3NH_2), disilazane ($(SiH_3)_2NH$) and disilaneamine ($Si_2H_5NH_2$) [7]. Polymeric solids are suspected to result from such intermediates, with successive SiH_2 insertions resulting in films of higher Si and N content. These solids are known to transform to silicon nitride under prolonged heating.

RESULTS AND DISCUSSION

Figure 2 is a TEM cross section view of a photolytically grown nine-layer a-Si/a-Ge structure. The average thickness of the first, third and fourth a-Ge layers is 54 (±2) Å, while for the four a-Si layers the average thickness is 107 (±4) Å. The thickness of successive layers was controlled by keeping the product of laser power and deposition time a constant for corresponding layers. The second a-Ge layer was deposited with the power-time product increased by ~24%, resulting in a layer 30% thicker (70 Å) than the average. These results illustrate the precise control over layer thickness, and the very sharp boundaries between layers, that can be achieved by laser photolysis. The HeNe reflectivity signal was monitored during deposition and was compared with model calculations. The experimental and calculated reflectivities were in semi-quantitative agreement (i.e., relative heights of successive reflectivity peaks and valleys were usually in the correct relationship), as a function of layer thickness. However, we must emphasize again that quantitative differences did occur between the calculated and actual reflectivities, presumably because n and k values for a-Si and a-Ge were not sufficiently well known under our deposition conditions. Nevertheless, these results show that very high precision can be maintained during photolytic deposition of amorphous superlattice structures, and that

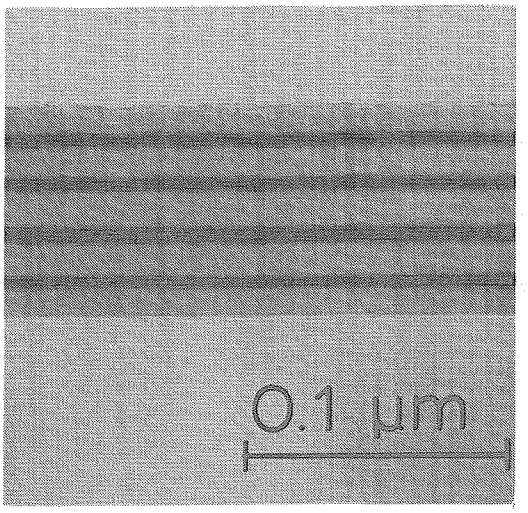

Fig. 2. Nine-layer a-Si/a-Ge structure deposited on (100) c-Si by ArF laser photolysis at 250°C.

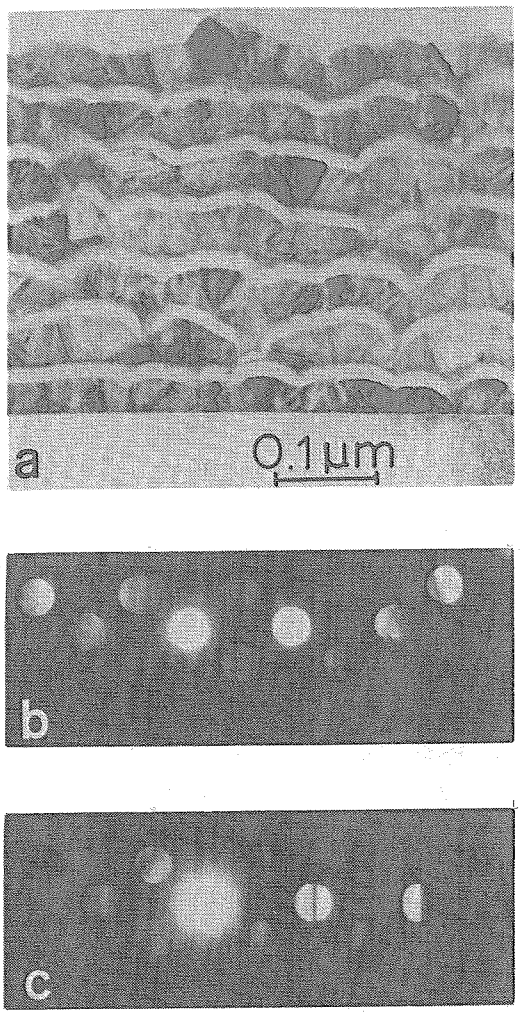

Fig. 3. (a) Fourteen-layer poly-Ge/a-Si structure deposited at 390°C, together with diffraction patterns illustrating epitaxial orientation of the bottom Ge layer (b) with the (100) c-Si substrate (c).

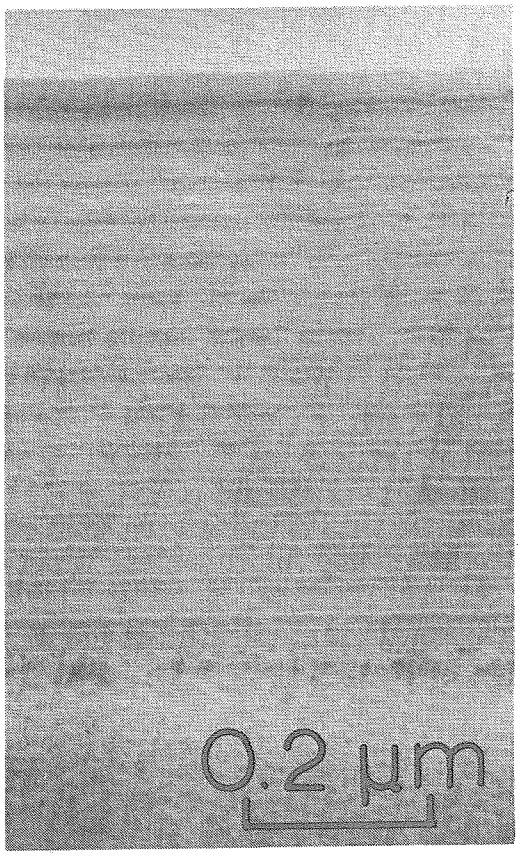

Fig. 4. TEM cross section view of 32-layer Si_3N_4/a-Si amorphous superlattice structure deposited by ArF laser photolysis at 350°C. Strong Fresnel fringe contrast is seen at the Si/Si_3N_4 interfaces.

model calculations provide at least semi-quantitative on-line verification that deposition is proceeding correctly.

Figure 3 shows the seven-period Ge/Si structure in which the Ge layers were deposited pyrolytically. In this case, the 390°C deposition temperature resulted in crystallization of all of the Ge layers, and in some resultant buckling of the multilayered structure when crystallization occurred. However, the bottom Ge layer is epitaxially oriented with the (100) c-Si substrate, though it still contains large numbers of twin boundaries. The Ge layers are 330 (±70) A thick, while the photolytic a-Si layers are about 130 (±12) A thick, again with very sharp boundaries and uniform thicknesses.

Figure 4 illustrates the result of photolytic deposition of a 32-layer (16-period) superlattice in which amorphous semiconductor (a-Si) and ceramic (Si_3N_4) layers are alternated. The overall thickness of the complete structure is about 6,260 A. After the first layer, the a-Si layer thicknesses

are 133 (±4) Å, while the Si_3N_4 layer thicknesses are 266 (±20) Å, as determined from TEM cross-section views. The optical reflectivity signal that was calculated before deposition of this structure gave an accurate picture of the relative heights and depths of successive reflectivity minima and maxima, respectively. However, the depth of modulation of the experimental reflectivity signal was still somewhat larger than in the calculations, which were based on optical parameters of single-layer a-Si and Si_3N_4 films that had been deposited in earlier experiments at temperatures that were only slightly different than the actual superlattice deposition temperature of 350°C. Thus, at this time we cannot rule out the possibility that at least part of the modulation of the reflectivity signal was due to interactions (interdiffusion, chemical reactions) occurring at or near the interface between alternate layers.

SUMMARY AND CONCLUSIONS

Because film deposition is controlled photochemically and not thermally, laser photolysis has certain advantages for the fabrication of artificially structured (multilayered) materials, as follows. (1) Film deposition can be carried out at low temperatures, minimizing dopant and impurity diffusion and resulting in atomically sharp interfaces. (2) The laser photon fluence provides excellent "on-off" control over film deposition. The use of high repetition rate pulsed excimer lasers results in precise "digital" control over film thickness, at the sub-monolayer level on average (per laser pulse), while maintaining attractive overall deposition rates. Since the film deposition rate also can be monitored optically with comparable resolution, then actual control over film growth can be achieved at the monolayer level. (3) The photolytic film growth concept appears to be broadly applicable to the growth of semiconductor, ceramic (dielectric) and metal thin films, using a variety of precursor gases, and thus to fabrication of a wide variety of multilayered structures.

ACKNOWLEDGMENTS

We would like to thank P. H. Fleming, J. T. Luck and C. W. Boggs for their assistance with sample preparation. This work was sponsored by the Division of Materials Science, U.S. Department of Energy under Contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

REFERENCES

1. See D. Eres, D. H. Lowndes, D. B. Geohegan, D. N. Mashburn and S. J. Pennycook, "Laser Photochemical Growth of Amorphous Silicon at Low Temperatures and Comparison with Thermal CVD," Symposium B of this meeting.
2. U. Itoh, Y. Toyoshima, H. Onuki, N. Washida and T. Ibuki, J. Chem. Phys. 85, 4867 (1986).
3. K. K. King, V. Tavitian, D. B. Geohegan, E.A.P. Cheng, S. A. Piette, F. J. Scheltens and J. G. Eden, Mat. Res. Soc. Symp. Proc. 75, 189 (1987).
4. T. Motooka and J. E. Greene, J. Appl. Phys. 59, 2015 (1986).
5. V. M. Donnelly, A. P. Baronavski and J. R. McDonald, Chem. Phys. 43, 271 (1979).
6. K. Watanabe, J. Chem. Phys. 22, 1564 (1964).
7. C.-H. Wu, J. Phys. Chem. 91, 5054 (1987).