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HIGH-SPEED EPITAXY USING SUPERSONIC MOLECULAR JETS

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HIGH-SPEED EPITAXY USING SUPERSONIC MOLECULAR JETS

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ABSTRACT

This paper discusses the use of supersonic jets of gaseous source molecules in thin film growth. Molecular jets in free form with no skimmers or collimators in the nozzle-substrate path were used in the investigation of basic film growth processes and in practical film growth applications. The Ge growth rates were found to depend linearly on the digermane jet intensity. Furthermore, the film thickness distributions showed excellent agreement with the distribution of digermane molecules in the jet. High epitaxial Ge growth rates were achieved on GaAs(100) substrates by utilizing high-intensity pulsed jets. The practical advantages and limitations of this film growth technique are evaluated, based on the results of microstructural and electrical measurements of heteroepitaxial Ge films on GaAs(100) substrates.

INTRODUCTION

Over the past decade, new film growth methods have been developed that extend control over a wider range of growth parameters, and consequently provide ways to grow better thin films and more sophisticated artificially structured materials. For example, the kinetic restrictions embodied in atomic (or molecular) layer epitaxy have demonstrated considerable success in controlling the growth of compound semiconductors at the monolayer level [1]. It has been claimed that the application of surface-active species in heteroepitaxial film growth prevents island growth by altering the interface energetics through adsorption of a third species which reduces the surface free energy [2]. Similarly, the driving force behind most other innovations in film growth methods is the search for a higher degree of external control over the process.

Despite the fact that gaseous sources have numerous advantages over elemental sources used in molecular beam epitaxy (MBE), they are not widely used in the MBE environment for the growth of group IV heterostructures because of the poor understanding of the underlying growth processes. The main advantage of using gaseous molecules is that they can provide much higher pressures for beam formation than the evaporative oven sources used in MBE, translating into higher beam fluxes and potentially higher film growth rates.

A supersonic free jet is a primitive beam source that combines the directional advantages of a beam growth method with the high intensities available from gaseous sources. A supersonic molecular jet is generated by expanding a binary gas mixture through a small nozzle orifice from a high stagnation (reservoir) pressure into a continuously pumped vacuum chamber. The gas mixture consists of a small amount (5%) of heavy molecules "seeded" (mixed) into a lighter inert carrier gas such as helium. During the expansion the random thermal motion of molecules is converted into a directional flow along the expansion axis, resulting in a strongly forward-peaking intensity distribution [3].

We have utilized both continuous and pulsed molecular jets to address several different aspects of Ge film growth from digermane molecules. The

excellent agreement between the intensity distribution of digermane molecules in continuous jets and the thickness distribution of films grown from these jets, leads to the conclusion that film growth occurs from the molecular jet, not from the steady-state digermane background pressure. Film growth rates from both continuous and pulsed jets were found to depend linearly on the digermane intensity. The reduction of the average gas load by operation in pulsed mode allows high intensity jets to be used even with relatively modest pumping speed. The resulting high growth rates were utilized to investigate the role of growth kinetics in epitaxial Ge growth on GaAs (100) substrates, by comparison of materials properties at different growth rates. My goal in this paper is to inspire participation in an exciting field of fundamental and applied research by briefly reviewing a few of our recently published results [4,5] and presenting some interesting new findings.

EXPERIMENTAL

Supersonic molecular jets were generated by expansion of a gas mixture containing 5% digermane (Ge_2H_6) in a helium carrier gas. For continuous jets, the intensity of digermane molecules at the substrate was varied by changing the distance between the nozzle and the substrate. At a fixed volume flow rate the intensity should fall with the square of the distance [6]. This behavior was confirmed by experiments at several distances. Because operation at high intensities requires high pumping speed, continuous jets were only suitable for investigation of film growth at the lower end of the growth rate range. The pumping speed requirements for generating high intensity jets were met by operating in a pulsed mode. The digermane intensity was changed by changing the reservoir pressure.

Continuous molecular jets were operated with a 0.125 mm diameter nozzle, a reservoir pressure of 120–140 Torr and a steady-state chamber pressure in the low 10^{-4} Torr range. For a 10–40 mm nozzle-to-surface distance these parameters yield digermane intensities of 10^{16} – 10^{18} molec/cm²s [6]. With reservoir pressures up to 1500 Torr, molecular jets having instantaneous intensities on the order of 10^{20} molec/cm²s were generated by pulsed operation from a 0.5 mm diameter nozzle. Pulse durations from 500 microseconds to 250 milliseconds were used.

Gas phase characterization of molecular jets was conducted by mass spectrometry in a differentially pumped two-chamber system. The side chamber housing the mass spectrometer was connected to the main chamber through a conical skimmer of 20 mm length with a 1 mm diameter orifice. The molecular jet was sampled at several positions downstream from the nozzle by monitoring the intensity of the mass peaks of various digermane fragments. Samples were taken along the centerline (the direction perpendicular to the plane of the nozzle orifice), and off-center along a direction perpendicular to the centerline. These data were used to determine the radial intensity distribution of digermane molecules in the molecular jet.

Ge films were grown from free jets with no skimmer or collimator inserted between the nozzle and the substrate. The substrates were heated in the temperature range from 400 to 700°C. Experimental details concerning film growth monitoring and substrate preparation have been given elsewhere [5].

RESULTS

The radial intensity distributions of both helium carrier gas and digermane molecules in continuous jets were measured at several nozzle-to-substrate distances within a 10–30 mm range. As shown on Fig. 1, an $I_0 \cos^m \theta$ function gave a good fit for both helium (with $m=15$) and digermane (with $m=22$) intensity distributions. The functional form of the digermane distributions in the jet was confirmed from several different digermane monoatomic and molecular fragments.

Figure 1. Normalized intensity distributions of the helium carrier gas (open circles) and digermane molecules (solid circles) in a continuous jet. The solid line represents a fit to $I_0 \cos^m \theta$ with $m=15$ for helium and $m=22$ for digermane distributions at a nozzle-to-substrate distance of 13 mm.

Ge films were grown on Si (100) from continuous jets with fixed volume flow rate in a nozzle-to-substrate distance range of 10–50 mm. The deposition rate dependence on digermane intensity shown on Fig. 2 was mapped out by changing the distance between the nozzle and the substrate. The scaling of deposition rates with the square of the distance between the nozzle and the substrate indicates that the growth rates are linearly proportional to the digermane intensity in the jet.

As illustrated by Fig. 3, the Ge film thickness distributions showed excellent agreement with the distribution of digermane molecules in the jet. Contributions to film growth from the steady-state chamber (background) pressure were observed only at large (over 30 mm) nozzle-to-substrate distances, for which the intensity in the jet was comparable to the impingement rate from the chamber background gas. Film growth from the background gas was manifested by broadening of the thickness distributions in the "wing" region where the intensity from the jet was lowest. However, Fig. 4 illustrates that good

Figure 2. Ge thin film deposition rates from continuous jets on Si (100), as a function of the reciprocal distance squared between the nozzle and the substrate. The distance is expressed in nozzle diameter units of $D=0.125$ mm. The solid line represents a fit to the data with the growth from the background (included in the dashed line) subtracted.

Figure 3. Normalized film thickness distribution for a Ge film on Si (100) given by solid circles, at a nozzle-to-substrate distance of 13 mm. The solid line represents a fit to the distribution of digermene molecules in the jet with $m=22$.

agreement with digermane intensity distributions could still be obtained by simply subtracting the small, steady-state background contribution to film growth.

Significantly higher instantaneous digermane intensities were obtained by operating the jet in a pulsed mode. The linear dependence of the Ge film growth rate on digermane intensity was confirmed for digermane intensities up to the high 10^{19} molec/cm²s range. The high intensity of digermane molecules at the substrates translates into Ge growth rates that are much higher (~ several μ m per minute) than attainable by presently available growth methods.

The high digermane intensities, along with the versatility of this growth technique in changing average growth rates over a wide range, were utilized to investigate the effect of growth kinetics on thin film quality. Microstructural

Figure 4. Normalized film thickness distributions for a Ge film grown on Si (100) at a nozzle-to-substrate distance of 24 mm, including growth from the background (open circles) and with the growth from the background subtracted (solid circles). The solid line represents a fit to the distribution of digermane molecules in the jet with $m=22$.

and electrical properties of epitaxial Ge films grown on GaAs (100) at average growth rates from 10 nm/min to over 1100 nm/min were investigated. Transmission electron microscopy (TEM), Rutherford backscattering spectroscopy (RBS), and x-ray double crystal diffraction (XDCCD) revealed high quality epitaxial Ge films (irrespective of growth rates) that were free of extended defects and misfit dislocations [5]. However, films grown slowly (10 nm/min) had rough surfaces characteristic of film growth by island formation. At high growth rates (1100 nm/min), a dramatic reduction of islanding was observed. The roughness at intermediate growth rates was found to be in inverse relationship with the growth rates [5].

Another consequence of rapid growth is a marked improvement in electrical properties. Ge films grown on GaAs (100) are either n-type or p-type as a result of autodoping from the substrate. The switch in carrier type, from n-type to p-type,

is a consequence of compensation, and the temperature at which it occurs is a function of growth rates. For Ge films grown rapidly [5] at 1100 nm/min this switch occurred above 600°C; in contrast, MBE-grown Ge films [7] turn p-type around 440°C. Films grown from molecular jets at slow growth rates (comparable to MBE rates) exhibited the same carrier type and carrier concentration as the MBE-grown material. In general, molecular jet-grown Ge films were less compensated, and consequently had higher carrier mobilities, than the MBE-grown material [5].

SUMMARY AND CONCLUSION

Supersonic expansions were used in the form of free jets as high intensity sources of digermane molecules for deposition of Ge thin films. High growth rates of epitaxial Ge on GaAs (100), free of extended defects and misfit dislocations, were achieved by utilizing pulsed jets. The differences in the properties of Ge films grown at low and high growth rates were interpreted in terms of interplay between thermodynamics and kinetics. Rapid growth provides a means to reduce or eliminate the deleterious effects of such processes as surface roughening, autodoping and impurity incorporation, by shortening the time available for these processes to reach their thermal equilibrium state.

The rather complex growth process prevents us from constructing a comprehensive growth model for Ge film growth from digermane. However, our experiments provide enough data to introduce a few important aspects of a possible growth model. Thin film growth from digermane occurs as a result of a heterogeneous surface reaction. No evidence for a contribution from homogeneous gas phase processes was observed. It was demonstrated that film growth occurs from molecules supplied directly by the jet, probably as a consequence of a single collision with the substrate surface. The first-order growth behavior suggests that the rate limiting process in Ge film growth is chemisorption occurring immediately upon impact with the surface, rather than chemisorption through a precursor-mediated reaction. In such direct chemisorption reactions the incident translational energy of the impinging molecules was shown to significantly increase the reaction probability with some metal surfaces [8].

Translational activation of surface chemical reactions is best investigated by utilizing supersonic expansions to generate translationally hot neutral molecules. Furthermore, supersonic expansions can be used to tune the translational energy and map out the reaction probability as a function of incident translational energy. Thus, supersonic molecular jets and supersonic molecular beams provide an additional parameter (translational energy of impinging molecules) for external control of the film growth process. Experiments that investigate the enhancement of Ge thin film growth rates from digermane molecules with superthermal translational energies are presently under way in our laboratory.

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