CONF-8706152--3

DIRECT FORMATION OF THIN FILMS AND EPITAXIAL OVERLAYERS AT LOW TEMPERATURES USING A LOW-ENERGY (10–500 eV) ION BEAM DEPOSITION SYSTEM*

R.A. ZUHR, G.D. ALTON, B.R. APPLETON, N. HERBOTS,† T.S. NOGGLE, AND S.J. PENNYCOOK
Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA
†Present address: Massachusetts Institute of Technology, Cambridge, MA 02139 USA

CONF-8706152--3

DE87 012291

ABSTRACT

A low-energy ion beam deposition system has been developed at Oak Ridge National Laboratory and has been applied successfully to the growth of epitaxial films at low temperatures for a number of different elements. The deposition system utilizes the ion source and optics of a commercial ion implantation accelerator. The 35 keV mass- and energy-analyzed ion beam from the accelerator is decelerated in a four-element electrostatic lens assembly to energies between 10 and 500 eV for direct deposition onto a target under UHV conditions. Current densities on the order of 10 $\mu A/cm^2$ are achieved with good uniformity over a 1.4 cm diameter spot. The completed films are characterized by Rutherford backscattering, ion channeling, cross-section transmission electron microscopy, and x-ray diffraction. The effects of substrate temperature, ion energy, and substrate cleaning have been studied. Epitaxial overlayers which show good minimum yields by ion channeling (3–4%) have been produced at temperatures as low as 375°C for Si on Si(100) and 250°C for Ge on Ge(100) at growth rates that exceed the solid-phase epitaxy rates at these temperatures by more than an order of magnitude.

INTRODUCTION

With recent advances in the use of new and ever more precise artificially structured materials by the semiconductor industry has come increased interest in the direct deposition of such overlayers and heterostructures by mass- and energy-analyzed ion beams.[1–13] Direct ion beam deposition (IBD) at low energies has many of the advantages normally associated with other ion beam processes, such as high-purity, isotopic selectivity, precise control of dose, and control of the deposition energy and depth. In addition, with controlled deposition energies substantially higher than those encountered in molecular beam epitaxy (MBE) or chemical vapor deposition (CVD), IBD should be capable of producing films with unique materials properties. Bombardment by these more energetic ions will create damage, nucleation sites, enhanced diffusion, and altered adatom mobilities that could result in metastable phases, unique lattice structures, or low-temperature epitaxial growth. In order to study the processes governing the production of such thin films by IBD and to determine the effects of temperature and beam energy on both the film and the substrate, a deceleration lens system for low-energy IBD was developed at ORNL. The system is capable of producing microampere beams of any element at energies from 10 to 1000 eV. In the first part of this paper we will discuss the detailed operation of this lens system, including some of the problems associated with its use for thin film deposition, as well as possible solutions to these problems. In the second part of the paper we

---

*Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

will present the results achieved by IBD for a variety of different elements, with emphasis on semiconductors and the growth of epitaxial films at low temperatures.

DECELERATED ION BEAMS

The deceleration lens system

Low-energy ions for the current series of deposition experiments are produced by decelerating higher energy beams from a commercial ion implantation accelerator (Extrion 1000-200) to the desired energies using a specially designed deceleration lens system. The modified Freeman ion source of the implantation machine is operated at its minimum extraction voltage of 35 keV to give an isotopically pure beam of the desired element at this energy. As illustrated in Fig. 1, this beam is then mass- and energy-analyzed in a 90 degree magnet, passed through three stages of collimation and differential pumping and a 7 degree electrostatic neutral trap, and fed into the deceleration lens which is located in the UHV deposition chamber. The base pressure in the deposition chamber is in the 10^{-10} T range and rises to $1\text{–}2 \times 10^{-9}$ T during deposition. Pumping is provided by a combination of turbo-, cryo-, and ion pumps. The high voltage for decelerating the beam is taken directly from the source extraction power supply. This is important because it eliminates deleterious effects on the deposition energy caused by any source voltage variations that are slower than the beam transit time (on the order of 10 μs or 100 kHtz). The deceleration lens itself is made up of four elements (for simplicity only three are shown in Fig. 1), two apertures that collimate and focus the beam, a third aperture to suppress electrons in the beam, and a disk-shaped deceleration electrode in which the sample is mounted. The deceleration electrode also contains an electrical resistance heater capable of reaching sample temperatures of 900°C, and a Faraday cup for profiling the beam to insure uniform current density over the target. In this system, deceleration takes place immediately in front of the sample so that the low-energy ions need to be controlled only over the shortest possible distance. This

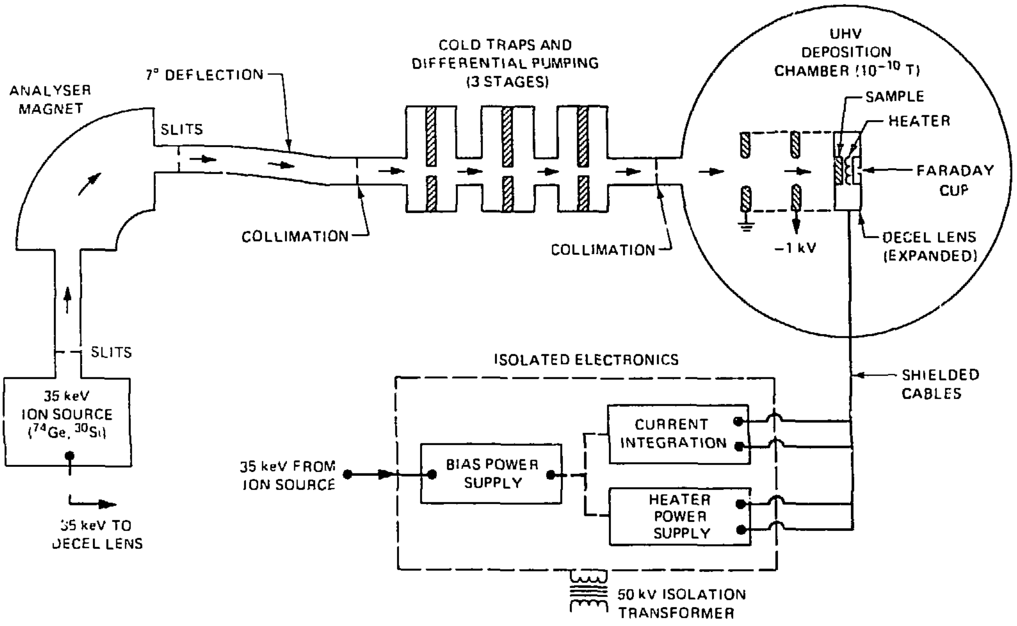


Fig. 1. Schematic diagram of the ORNL IBD system showing the 35 keV ion source, the beam transport hardware, and the UHV deceleration lens and associated electronics.

system can produce currents of 10–50 μA over a 3 cm^2 beam spot for virtually any element at the energies of interest for IBD. Currents from a single isotope may be somewhat lower, depending upon the isotopic abundance contained in the source material. Currents of 10–20 μA are readily available for ^{30}Si (abundance = 3.09%) from a natural Si source. Typical current densities during deposition are 5–10 μA/cm^2, resulting in deposition rates on the order of a few monolayers per minute.

Limitations of deceleration systems

Maintaining precise control of a low-energy ion beam with high-current density is a difficult problem. In the present lens system deceleration takes place as close to the sample as possible, yet there are still limitations on the current density that can be passed to the target, ≈ 10 μA/cm^2. As the input current to the lens is increased, less and less of the added current reaches the target. The reasons for this are Coulomb repulsion in the beam and defocusing in the lens at these very low longitudinal energies. Order of magnitude improvements in current density would probably require some degree of beam neutralization, which would negatively affect current integration and has not been considered for this lens system, but may be necessary for commercial applications of IBD. Additional causes of the limited current density are the beam scanning, which is done to insure uniformity, non-optimal beam optics, and the beam energy distribution, which is illustrated in Fig. 2. This energy distribution was measured by using the system as a retarding field analyzer and measuring the current to the target as a function of deposition energy (right-hand scale). Corrections for secondary electrons created by the rejected fraction of the beam are included. The left-hand scale gives the fraction of the total current (% per eV) that reaches the sample at each nominal energy. Although most of the current is concentrated near "zero", which corresponds to the maximum energy on the target for a given deceleration voltage, it is clear that there is a substantial ion flux that stretches more than 150 eV below that energy. Thus the energy distribution for any given deposition energy below 200 eV is not monoenergetic, but contains a low-energy tail that extends to zero energy. In addition to decreasing the flux to the sample at lower energies, this broad distribution leads to other problems. The low-energy component of the beam that does not reach the target is accelerated back up the beam line, where some of it, due to Coulomb effects and transverse velocity components in the original beam, strikes the last aperture electrode. These 35 keV ions result in sputtering and secondary electron emission from the electrode. Some of the sputtered particles, being predominantly neutrals, drift to the sample and produce contamination, while the secondary electrons are drawn to the electrode and contribute errors to the current integration. These problems have been alleviated by coating the final electrode with the element being used for the deposition so that the sputtered atoms merely contribute to the film, and by electrically isolating the sample from the deceleration electrode to minimize the effects of the secondary electrons on the dose calibration.

APPLICATIONS AND RESULTS

Preparation of semiconductor samples

All depositions on semiconductors were done on electronics-quality substrates that were chemically cleaned[14] immediately prior to insertion into the vacuum system. For successful epitaxial deposition it was necessary to carry out additional in-situ cleaning procedures. For Ge sputter cleaning with the self-ion and annealing at 600°C for one hour produced a surface that gave high-quality epitaxy. This procedure was not adequate for epitaxial growth on Si substrates, probably because the temperature was not high enough to completely anneal the sputtering damage. For Si, a procedure analogous to reactive ion etching was developed. The sample was chemically cleaned by directing a beam of low-energy Cl or F ions onto the Si surface at 600°C, followed by a brief (1/2 hr) anneal to remove any trapped atoms. Such a cleaning procedure resulted in epitaxial growth on Si.

Damage in Si substrates

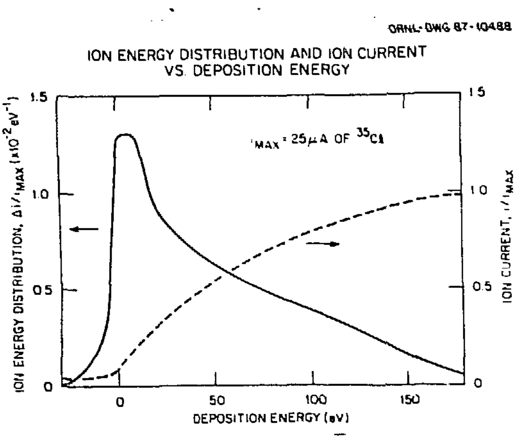
Anomalous damage has been observed in Si substrates under two different deposition conditions. For room temperature, depositions at energies above 100 eV, damage has been observed at depths up to 40 nm which is an order of magnitude beyond the range of such ions. This damage is believed to be due to radiation-enhanced diffusion. In the second case, for substrate temperatures above 400°C, a buried layer of dislocation loops extending from 50 to 150 nm below the original interface is observed for all deposition energies (see Figs. 5b, 8). The region between the damaged layer and the interface is defect free. In both cases the effect is seen only in Si, indicating a strong dependence on the characteristics of the material. More complete discussions of this damage have been published previously.[15—17]

Uniform continuous films

Under the conditions described above, it has been possible to deposit high-purity, uniform, continuous films for a variety of elements that show no evidence of islanding even for very thin (10 ML) deposits.[12] These films have uniformly sharp interfaces by TEM (<0.35 nm) and show no evidence of damage to the substrate for room temperature low energy (<65 eV) depositions. In addition, by varying beam energy and substrate temperature, either amorphous or polycrystalline films may be formed.[12]

Epitaxial growth

We have demonstrated previously that high-quality epitaxial films can be grown at temperatures lower than those normally used for epitaxial growth by MBE or CVD.[13,15] An example of such a film is given in Fig. 3, which shows backscattering spectra for an epitaxial ^{30}Si film grown on Si(100) at 400°C with a beam energy of 10 eV. Because of the mass difference between the ^{30}Si of the film and the natural Si, the film-substrate interface is sharply delineated in the spectra. This film is clearly epitaxial and has a good minimum yield of 3.6% on the <110> axis, although cross-section TEM indicates that such films are not completely free of extended defects. The growth rate for Si films grown by IBD at this temperature exceeds the measured solid-phase epitaxy (SPE) rate[18] by more than an order of magnitude, indicating clearly the positive effects of IBD on the epitaxial growth of Si. Films of similar quality have been grown for ^{74}Ge on Ge(100) at 375°C and ^{57}Fe on Ag(100) at 250°C. In the latter case, because the lattice constants differ by the square root of 2, the Fe lattice is rotated about the surface normal by 45° with respect to the underlying Ag, so that, in the surface plane, the <110> axis in the Fe lies along the <100> axis in the Ag. In addition, heteroepitaxial growth of ^{74}Ge on a Si(100) substrate has been achieved at 400°C without a graded interface. The quality of such films is not as good as in the homoepitaxial case, showing a minimum yield of ≈ 12%, as illustrated in the backscattering spectra of Fig. 4.



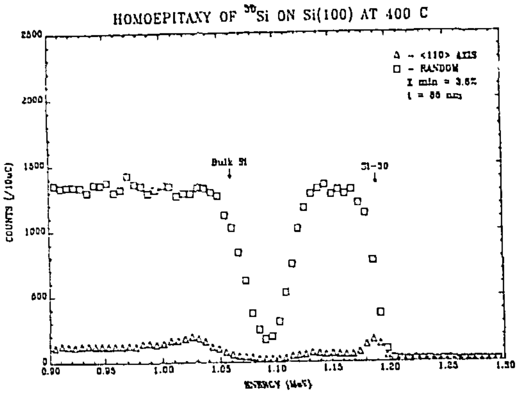


Fig. 2. Relative beam current reaching the sample (-----), and relative ion energy distribution (-----) as functions of deposition energy for a 25 μA Cl beam. The left-hand scale gives the % of the total current per eV. For a given deposition energy below 200 eV the energy distribution is peaked at that energy ("zero" on this scale) with a tail extending to zero energy.

Fig. 3. Aligned and random RBS spectra for an epitaxial layer of ^{30}Si grown on Si(100) at 10 eV and 400°C that has an excellent minimum yield (3.6%). The separation between the layer and the substrate in the figure is the result of the mass difference between ^{30}Si and natural Si.

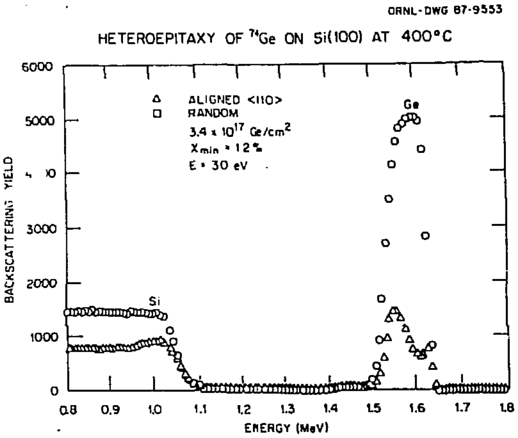


Fig. 4. Aligned and random RBS spectra for an epitaxial layer of ^{74}Ge deposited on a Si(100) substrate at 30 eV and 400°C. The high minimum yield for the Ge (12%) indicates damage in the film.

Limitations of Epitaxial Growth by IBD

In order to determine the temperature limits for epitaxial growth of semiconductors by IBD, a series of experimental depositions were performed in which the substrate temperature was stepped downward during the growth of the film. The results for such a stepped temperature experiment for ^{30}Si on Si(100) are illustrated in the backscattering spectra and cross-section TEM micrographs of Fig. 5. This film was deposited at an ion energy of 30 eV and a substrate temperature that started at 600°C and was decreased in steps to less than 250°C as indicated on the backscattering spectra of Fig. 5a, which compares random (□) and aligned <110> (Δ) spectra for this film. Note that with each decrease in temperature there is a corresponding decrease in the quality of the film as determined by ion

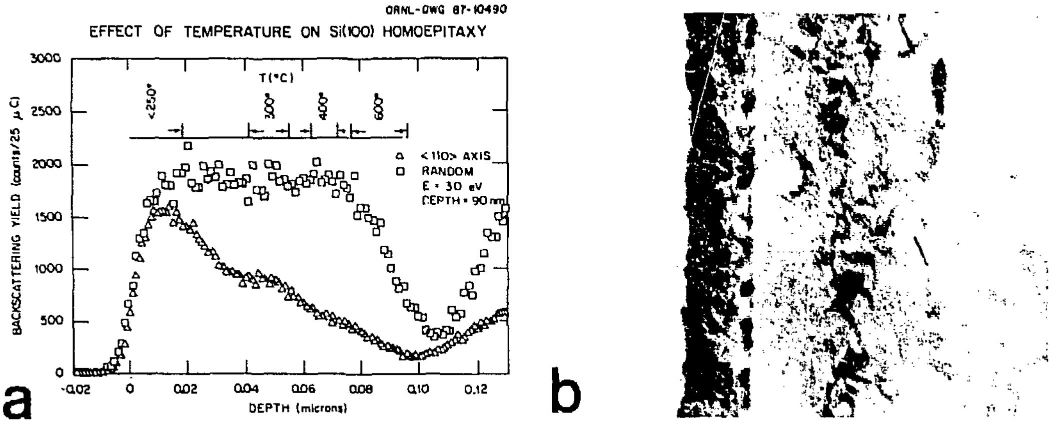


Fig. 5. RBS (a) and TEM (b) analyses of a 90 nm epitaxial layer of ^{30}Si grown on Si(100) at 30 eV with stepped decreases in temperature. The channeled spectrum (a) clearly shows a decrease in epitaxy with decreasing temperature. The corresponding micrograph (b) shows an increase in defect density going from the interface to the surface, also with decreasing temperature.

channeling, indicating that epitaxial growth by IBD is not a completely athermal process. Although the film still shows evidence of epitaxy at temperatures below 250°C, the quality of the film at this temperature has deteriorated badly, as indicated by the minimum yield of over 0.85. There is evidence that deposition at the lower temperatures increases the damage in material previously deposited at higher temperatures, since the channeling here has deteriorated at 400°C, a temperature at which excellent quality epitaxy has already been demonstrated (see Fig. 3). The TEM results (Fig. 5b) show a rather badly defected film, with a noticeable increase in the amount of damage going from the substrate to the surface, that is, with decreasing temperature.

Results for a similar experiment on the temperature limits for the homoepitaxial growth of Ge films by IBD are shown in Fig. 6. Here the temperature was lowered from 440°C at the start of a ^{74}Ge deposition onto Ge(100), to less than 250°C at the end. In this case the channeling results (Fig. 6a) show an excellent minimum yield of less than 3.5% with no deterioration in film quality as the temperature is decreased. Examination by cross section TEM (Fig. 6b), however, shows evidence that thermal processes are important to the epitaxial growth. The first half of the film shows a high degree of perfection, but extended defects are observed nearer the surface where the deposition temperature was lower. That the epitaxial growth of Ge by IBD is also temperature limited is confirmed by the results of Fig. 7. Here the deposition was again begun at elevated temperature, but the heater was turned off and the sample was allowed to cool to room temperature. As can be seen from the backscattering spectra, this sample shows essentially no epitaxy by channeling.

It has been shown that the growth of quality epitaxial films by IBD is limited by temperature for both Si and Ge, with Ge growing effectively at substantially lower temperatures. If we make the simple assumption that the temperature limits for epitaxial growth scale with the melting points, then the experimentally observed limit for Si, ≈ 650 K, multiplied by the ratio of the melting points, 1210 K/1683 K, gives a lower limit for Ge epitaxy of ≈ 470 K, approximately equal to the temperature at which Ge epitaxial growth was observed to deteriorate. It thus appears that comparable phenomena are governing the homoepitaxial growth processes under IBD for both Si and Ge.

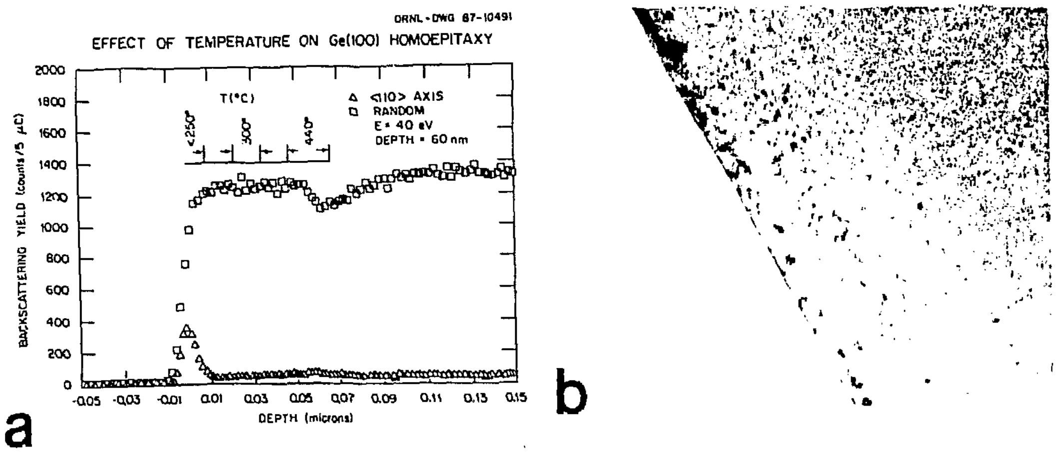


Fig. 6. RBS (a) and TEM (b) analyses of a 60 nm epitaxial layer of ^{74}Ge grown on Ge(100) at 40 eV with stepped decreases in temperature. The channeled spectrum shows a high degree of epitaxy throughout the film. The micrograph, although indicating excellent crystal quality in the first half of the film, shows defects beginning to form at the lower temperatures near the surface.

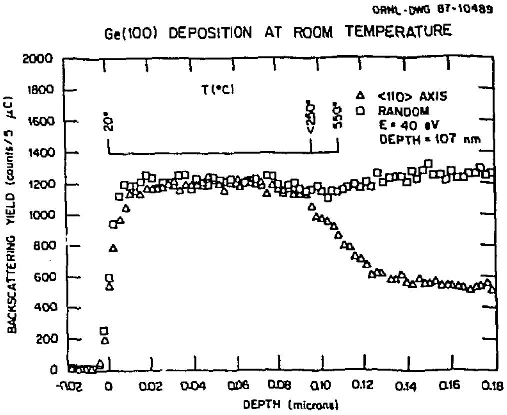


Fig. 7. Aligned and random spectra for a ^{30}Si film grown on Si(100) at 100 eV with decreasing temperatures. The channeled spectrum shows a lower degree of epitaxy than the 30 eV deposition of Fig. 5.

For the case of silicon homoepitaxy, a sufficient amount of data has been collected to provide some insight into the role of ion beam energy in the IBD growth process. Epitaxial overlayers of ^{30}Si on Si(100) showing similar qualities as measured by backscattering and TEM have been produced for ion energies from 10 to 65 eV. In general, no effect on the minimum yield has been seen for different energies within this range, and only small differences have been observed in the TEM micrographs. Such differences are illustrated in Fig. 8, where cross-section TEM micrographs of Si films deposited on Si(100) at 20 eV (a) and 40 eV (b) and 600°C are compared. The film deposited at the higher energy, 40 eV, Fig. 8b, shows more twinning near the interface and a higher density of threading dislocations extending to the surface. In both micrographs a comparable band of buried damage is observed from 50 to 150 nm below the original interface. The effects of ion energy on the low-temperature limitations of epitaxial growth are demonstrated in Fig. 9. Here a deposition comparable to that of Fig. 5 was made with the temperature being reduced during deposition from 600°C to less than 250°C, but with an ion energy of 100 eV. The channeling spectrum indicates epitaxy only at the highest temperatures. A comparison

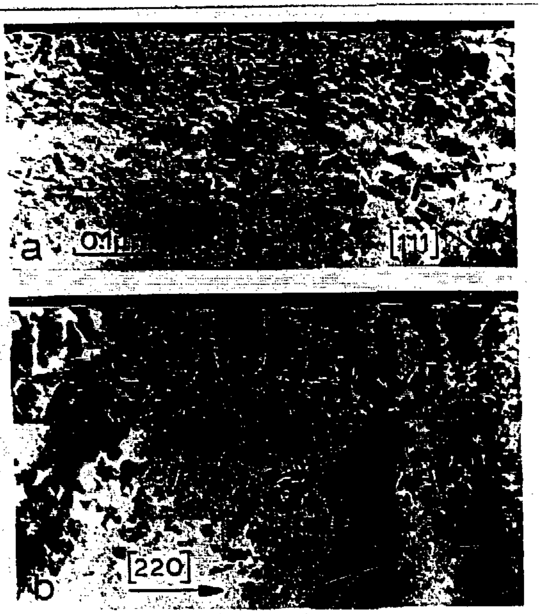


Fig. 8. Comparison of cross-section TEM micrographs of ^{30}Si films grown on Si(100) at 600°C with energies of 20 eV (a) and 40 eV (b). A layer of buried dislocation loops is evident in both cases.

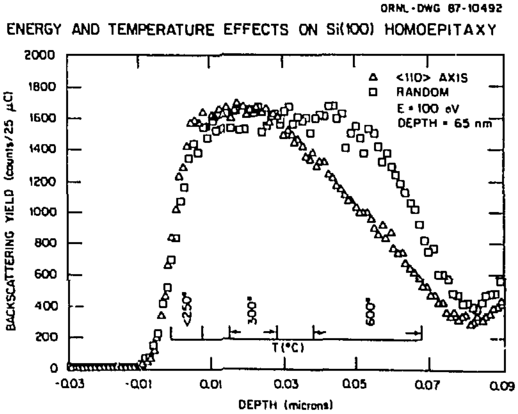


Fig. 9. Aligned and random spectra for a ^{74}Ge film grown on Ge(100) at 40 eV with the temperature decreasing from 550°C to room temperature. The channeled spectrum shows a complete deterioration of the epitaxy below 250°C.

with the ion scattering spectra of Fig. 5, which was a 30 eV deposition covering the same temperature range, indicates that the higher beam energy has been detrimental, rather than conducive, to epitaxial growth. The advantages of higher ion energy in terms of increased surface mobility, the creation of nucleation sites, and radiation enhanced diffusion have been overcome, for the purposes of epitaxial growth, by the increased rate of introduction of damage.

CONCLUSIONS

Ion beam deposition has been shown to be an effective technique for producing uniform, continuous, high-purity, monoisotopic films and heterostructures of a variety of elements at moderate deposition rates. The control of the deposition parameters that is inherent in this technique makes it possible to produce elementally sharp interfaces, to control the production of damage, and to tailor the crystallographic characteristics of the film and substrate. In a given temperature regime that is material dependent, IBD permits high-quality epitaxial growth of semiconductors at rates more than an order of magnitude faster than SPE rates for that material. Energies below 100 eV have been shown to give the best results for homoepitaxy in semiconductors, and low temperature limits for quality epitaxial growth at moderate rates in the present system have been found to be ≈ 375°C for Si(100) and ≈ 200°C for Ge(100). Because of its controlled deposition characteristics, IBD offers unique opportunities for the study of fundamental aspects of ion beam damage, interfaces, ion beam mixing, diffusion, and epitaxial growth.

REFERENCES

1. J. Amano, P. Bryce, and R.W.P. Lawson, J. Vac. Sci. Technol. 13 (2), 591 (1976).
2. J. Amano and R.W.P. Lawson, J. Vac. Sci. Technol. 15 (1), 118 (1978).
3. J. Amano, Thin Solid Films 92, 115 (1982).
4. K. Yagi, S. Tamura, and T. Tokyama, Jpn. J. Appl. Phys. 16, 245 (1982).
5. T. Tsukizoe, T. Nakai, and N. Ohmae, J. Appl. Phys. 42, 4770 (1977).
6. T. Tokuyama, K. Yagi, K. Miyake, M. Tamura, N. Natsuaki, and S. Tachi, Nucl. Instrum. Methods 182/183, 241 (1981).
7. G.E. Thomas, L.J. Beckers, J.J. Vrakking, and B.B. de Koning, J. Cryst. Growth 56, 557 (1982).
8. K. Miyake and T. Tokuyama, Thin Solid Films 92, 123 (1982).
9. P.C. Zalm and L.J. Beckers, Appl. Phys. Lett. 41 (2), 167 (1982).
10. I. Yamada, H. Inokawa, and T. Takage, Nucl. Instrum. Methods B 6, 439 (1985).
11. N. Herbots, B.R. Appleton, T.S. Noggle, R.A. Zuhr, and S.J. Pennycook, Nucl. Instrum. Methods B 13, 250 (1986).
12. N. Herbots, B.R. Appleton, S.J. Pennycook, T.S. Noggle, and R.A. Zuhr, in *Beam-Solid Interactions and Phase Transformations*, edited by H. Kurz, G.L. Olson, and J.M. Poate (Materials Research Society, Pittsburgh, Pennsylvania, 1986), p. 369.
13. B.R. Appleton, S.J. Pennycook, R.A. Zuhr, N. Herbots, and T.S. Noggle, Nucl. Instrum. Methods B (in press, 1987).
14. E.D. Marshall, C.S. Wu, C.S. Pai, D.M. Scott, and S.S. Lau, Mat. Res. Soc. Symp. Proc. 47, 161 (1985).
15. R.A. Zuhr, B.R. Appleton, N. Herbots, B.C. Larson, T.S. Noggle, and S.J. Pennycook, J. Vac. Sci. Technol. A (in press, 1987).
16. N. Herbots, B.R. Appleton, T.S. Noggle, S.J. Pennycook, R.A. Zuhr, and D.M. Zehner, in *Semiconductor-Based Heterostructures*, edited by M.L. Green, J.E.E. Balin, G.Y. Chin, H.W. Deckman, W. Mayo, and D. Narashinham (The Metallurgical Society, 1986), p. 335.
17. B.R. Appleton, R.A. Zuhr, T.S. Noggle, N. Herbots, and S.J. Pennycook, in *Beam-Solid Interactions and Transient Processes*, edited by S.T. Picraux, M.O. Thompson, and J.S. Williams (Materials Research Society, Pittsburgh, Pennsylvania, 1986, in press).
18. E.P. Donovan, F. Spaepen, D. Turnbill, J.M. Poate, and D.C. Jacobson, J. Appl. Phys. 57, 1795 (1985).