GaAs on Si結晶의 成長과 그 特性解析

°丁 世鎭, 成 萬永

高麗大學校 電氣工學科

Analysis and Growth of GaAs on Si

Se Jin Jeong, Man Young Sung

Dept. of Electrical Eng.
Korea University, Seoul, Korea.

Abstracts

A single-crystalline epitaxial film of GaAs has been grown on Si using an ionized cluster beam technique. The native oxide layer on the silicon substrate was removed at 550℃ by use of an accelerated arsenic ion beam, instead of a high-temperature desorption. During the growth the substrate temperature was maintained at 550℃. Transmission electron microscopy and electron diffraction data suggest that the GaAs layer is an epitaxially grown single-crystalline layer.

I. INTRODUCTION

In common practice today, there are several material growth techniques that are particularly suitable for the sequential growth of epitaxial thin films, which are required for the fabrication of compound semiconductor optoelectronic device structures. In general, these techniques can be classified into three different categories: molecular-beam epitaxy (MBE),[1-4] vapor phase epitaxy (VPE),[5-7] and liquid phase epitaxy (LPE).[8-10] Described in this paper are the preliminary results from yet another thin-film growth technique, known as ionized cluster beam (ICB) deposition,[11] which has recently been employed to grow an epitaxial thin GaAs film on Si.

ICB deposition is a technique which shares the advantages of "conventional" beam-assisted deposition, but may overcome some of its limitations. Although the actual mechanisms of ICB deposition have not yet been elucidated, it is believed that they are similar to ion beam deposition in that energy is supplied to the growing film surface by an ion beam thus allowing for localized atomic motion and rearrangements. There is, however, an important difference. The energy of an ionized cluster is shared by all atoms in the cluster so that individual atom energies are very low even when the individual clusters themselves contain substantially high energies. Thus, sufficient energy can be supplied to a localized region to stimulate atomic motion, but without any one atom gaining sufficient energy to become implanted or to create point defects. In principle, therefore, ICB deposition offers a novel way to produce thin films, and for some applications, it may have important advantages over conventional MBE or beam-assisted deposition methods.

The application of ICB deposition to the growth of high-quality films has, indeed, been demonstrated. Takagi and co-workers have shown, for example, that epitaxial Al films could be grown on Si at temperatures as low as room temperature.[12] They have reported other successes with a variety of source materials and substrates; these include metals, intermetallic compounds, semiconductors, oxides, nitrides, carbides, fluorides, and even organic materials.[13,14] In most of this work, the main objective was to produce highly adhesive, smooth coatings; although with a few materials, the Takagi group was also able to grow thin films of controllable crystalline structure and optical properties.[14] In spite of these apparent "successes," the work of Takagi *et al.* has been controversial ever since it was first reported in 1972, mainly because they have failed to characterize their cluster beams for size and energy distributions. Moreover, there has been very little research on determining what films can be grown on what substrates, the conditions of growth, and very importantly, the quality of the films and the perfection of the interfaces.

Our work with ICB's at the University of Illinois, which began just over three years ago, has concentrated mainly on compound semiconductors, metals with known applications in microelectronics, and catalytic materials. The principal objective of this work has been twofold: (i) to study the fundamental physical processes controlling the cluster formation and (ii) to evaluate the unique capabilities, as well as limitations, of the ICB technique for various scientific applications of current interest. The results that we have obtained to date are still preliminary; nevertheless, by growing an epitaxial GaAs film on Si at a low temperature using a dual-beam configuration, by producing Zn and Al clusters, and by fabricating crystalline catalytic Ni particles having sizes in the range 10–1000 Å, we have clearly demonstrated that the ICB technique is both promising and versatile.

Presented in this report is an account of the work on the growth of GaAs thin films on Si using the ICB deposition. The apparatus, specifically designed and fabricated for the present work, and the experimental procedures used are described in Sec. II. The results obtained with the apparatus are presented and discussed in Sec. III, along with the microanalysis results of the grown films. Section IV contains the summary and concluding remarks.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

The ICB deposition (ICBD) system specifically constructed for the present study is shown in Fig. 1. Two separate crucibles, one for As and the other for Ga, are used to independently control the temperature of the source material in each crucible. In this respect, ICBD is similar to MBE.

The similarity between ICBD and MBE, however, stops here since in ICBD the crucible is covered with a cap having a small flow-constricting nozzle which allows one to maintain a much higher vapor pressure inside the crucible than that of MBE. It is because of this nozzle that the vapor coming out of the crucible adiabatically expands into a vacuum resulting in small aggregates of atoms, namely, "clusters." Once produced, these clusters are impact ionized using thermionic electrons, accelerated in an electric field, and delivered to a heated substrate for material deposition. The ratio of ionized to neutral clusters in the ionized cluster beam, the energy with which the ionized clusters impinge upon the substrate, the size of clusters, and the substrate temperature then become the parameters controlling the morphology, smoothness, and other properties of the growing film.

The ICBD system schematically illustrated by Fig. 1 is housed in a vacuum bell jar whose base pressure was typically 5×10^{-7} Torr for all the thin-film growth runs. A typical experimental sequence for the growth of GaAs on Si is as follows. First turn on the As crucible and heat the substrate to the desired temperature. Then turn on the ionizer and supply an acceleration field to the ionized As beam so that, when the energetic beam hits the Si substrate, it can remove the native SiO_2 layer. The energy of the As beam and the time duration over which it is directed onto the substrate therefore control the substrate cleaning. While cleaning is being done start heating the Ga crucible. The next step is to start the film growth process by lowering the As beam acceleration voltage to a desired value and opening the shutter to the Ga crucible. The GaAs thin films grown on the Si substrate using these procedures are shown and analyzed in the next section.

III. RESULTS AND DISCUSSION

GaAs thin films grown on a Si substrate under two different conditions are presented. Figure 2(a) shows a scanning electron microscopy (SEM) picture taken of a sample (sample A) prepared at an As crucible temperature of 300 °C, a Ga crucible temperature of 920 °C, an As ion acceleration voltage of 1 kV, and a substrate temperature of 550 °C. The Si substrate used was an *n*-type Si(100). The nozzles that served as the exit end of the source crucible were 1-mm diameter × 2-mm length for both the As and Ga crucibles. However, the Ga beam was not ionized. The total growth time was 10 h and the average growth rate was 3800 Å/h. Prior to the growth, the Si substrate was heated to and kept at 900 °C for 15 min to facilitate removal of the native oxide layer.

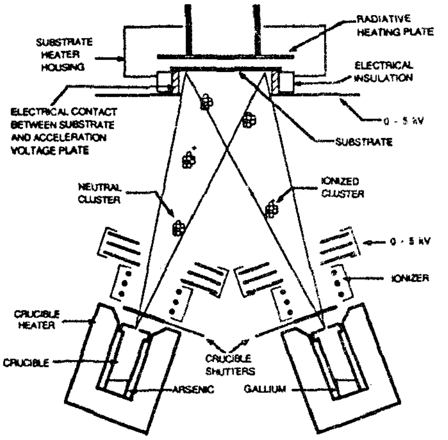

FIG. 1. Schematic of a dual-crucible ICBD system employed for the growth of an epitaxial GaAs thin film on Si.

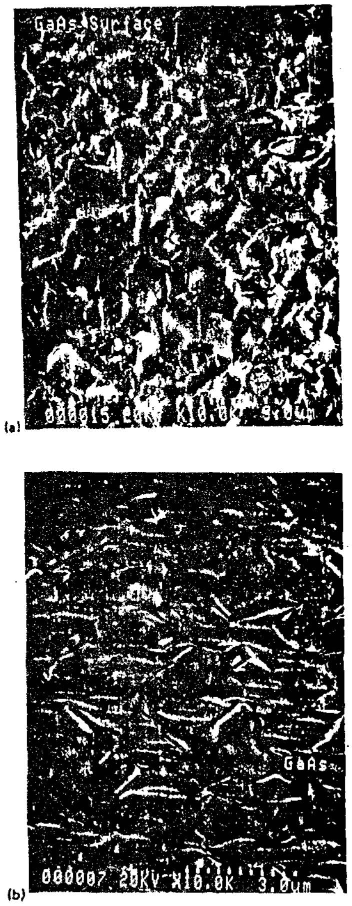

FIG. 2. SEM pictures of two GaAs films on Si grown under different conditions. The magnification is 10k ×. (a) Sample A: Prior to the growth, the Si substrate was heated to and kept at 900 °C for 15 min. (b) Sample B: Prior to the growth, the Si substrate was cleaned for 1 h using a beam of As ions accelerated to 1.5 kV.

The SEM picture of Fig. 2(a) indicates that the grown film is fairly smooth; however, x-ray diffractometer measurement (not presented) and a cross-section transmission electron microscopy (TEM) analysis [Fig. 3(a)] indicate that although it is of a preferred (111) orientation, the grown film is not single crystalline. As can be seen from Fig. 3(a), there is still a thin layer of SiO_2 remaining on top of the Si substrate. This means that because of the less than desirable vacuum condition (5×10^{-7} Torr) of the growth chamber, the thermal desorption method routinely employed by crystal growers to successfully remove native oxide in an UHV environment did not work in this case. As a result, GaAs was actually nucleated and grown on an amorphous substrate. Given the complete freedom in the nucleation orientation on an amorphous substrate, as most other cubic materials which are deposited on amorphous substrates do, the obtained GaAs on Si exhibits a columnar growth shown in Fig. 3(a) with a (111) preferred orientation.

To remedy this drawback, an attempt to remove the native oxide layer at a low substrate temperature was made by using an As ion beam accelerated to 1.5 kV. The GaAs thin film shown in Fig. 2(b) (sample B) was grown after the Si substrate was cleaned for 1 h using an accelerated As ion beam. During this cleaning, the As crucible temperature was maintained at 300 °C and the substrate temperature at 550 °C. The Ga crucible was operated without the nozzle during thin-film growth since the Ga beam was not ionized and, consequently, the use of a nozzle did not seem to be beneficial. Other than these differences, the rest of the growth conditions and procedures remained the same as those adopted for the sample shown in Figs. 2(a) and 3(a). The measured growth rate was found to be identical for the two cases.

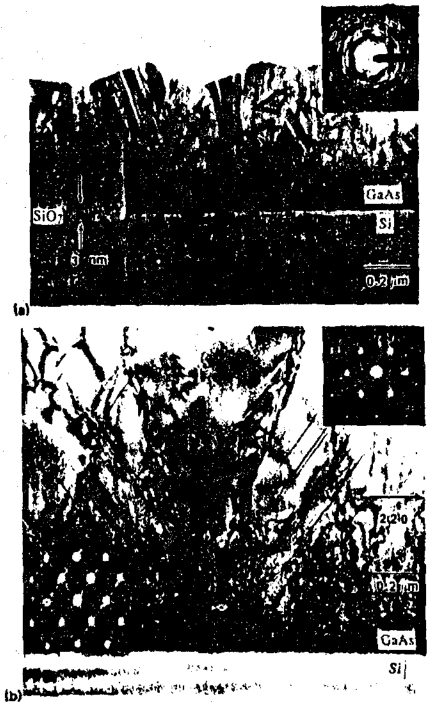

FIG. 3. TEM bright-field images of GaAs on Si for the samples shown in Fig. 2. (a) Sample A: An enlarged micrograph (lower left-hand inset) shows *that inadequate cleaning (utilizing a high-temperature thermal desorption)* leaves a SiO_2 layer about 30 Å thick along the GaAs/Si interface. As a result, GaAs deposited on becomes polycrystalline (upper right-hand inset). (b) Sample B: After the SiO_2 layer is removed by ionized As flux, single-crystalline epitaxial GaAs layer is deposited on Si substrates successfully.

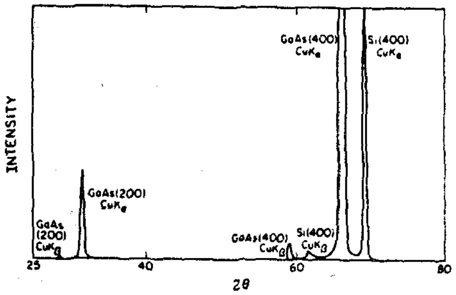

FIG. 4. X-ray diffraction data of sample B [Figs. 2(b) and 3(b)] indicating single-crystalline (100)GaAs layer grown on (100)Si.

As can be seen from Fig. 2(b), the surface of sample B, albeit imperfect, is smoother than that of sample A [Fig. 2(a)]. But more importantly, an x-ray analysis (Fig. 4) showed that the orientation of the grown film is (100)—same as the substrate. Furthermore, a TEM analysis, as shown by Fig. 3(b), indicates that the film is single crystalline and that the native oxide layer is no longer present.

As for the verification of the existence of clusters which may or may not have played an important role in the present work, a statement or two must be made to eliminate any misunderstanding. First of all, a direct cluster measurement was not made in the present work simply because such an apparatus could not be implemented inside the vacuum bell jar that housed the dual-crucible system used for the present work; however, at least two indirect proofs can be offered by way of stating that it was very likely that because of the size of the nozzle and the vapor pressure used for the work, As clusters were present, along with the single atoms, during the growth. The first indirect proof is that using a 2000-amu quadrupole mass spectrometer a beam of Al produced with a nozzle of 1-mm diameter and 2-mm length, same as the one used for the present work, was analyzed and the results showed that clusters as large as 10 atom were produced. Using the same-size nozzle Ni was deposited onto a copper-coated graphite TEM target and the analysis showed that clusters ranging in size from 10 to 1000 Å were produced in abundance.

For a detailed study of the ICB technique, there is, therefore, a strong need for a specially designed UHV system, similar to a state-of-the-art MBE system, that provides for convenient production and detection of multiple ICB's, controlled ionizations of ICB's and determination of their ionization state, tuning of the ICB energy, and finally *in situ* characterization of growing films. This was not done in the work of Takagi and, consequently, that work is highly debated in the film-growth community. Such an UHV system featuring multiple-source flanges, a reflection high-energy electron diffraction (RHEED) diagnostic, a 4000-amu quadrupole mass spectrometer, a load lock, and other auxiliary components has been under construction in our laboratory at the University of Illinois and is nearing completion. Using this state-of-the-art system, we plan to do *in situ* studies of various important issues pertaining to film growth with ICB's: the size and energy distribution of clusters, the mechanism by which the clusters interact with energetic electrons during their ionization, and the thin-film growth process after a partially ionized cluster beam has been delivered onto the substrate.

IV. SUMMARY AND CONCLUDING REMARKS

Preliminary results indicating the capability of the ICB technique to grow an epitaxial thin film of GaAs on Si have been presented. Of particular interest is the demonstration that the native oxide layer can be removed from Si at a low temperature (550 °C) using a beam of accelerated As ions. Because of this unique capability, the Si substrate temperature was never raised above 550 °C during the entire film-growth sequence. The issue of whether As clusters played a role, if any, in the present work was not resolved because of lack of appropriate diagnostics, although in conjunction with both the Al and Ni work that was done using different systems, it was observed that clusters could be produced with a similar setup (data not included in this paper). A state-of-the-art ICB system that can possibly resolve this and other fundamental issues, thus facilitating more rudimentary understanding of the ICB technique, has been fabricated and is nearing completion.

It is hoped that this new UHV system equipped with *in situ* diagnostics and convenient load lock will in time answer various important fundamental issues pertaining to the ICB technique. These include determining (i) the underlying physical processes of an energetic cluster impinging on a substrate, (ii) the relationship between the physical parameters of the ICB technique—cluster size, energy, ionization state, and substrate temperature—and the quality and nature of the film, (iii) the physical processes involved in producing the ICB, and (iv) the capabilities and limitations of the ICB method. We will carry out this research by performing studies of the cluster beam characteristics and their relationships to film growth, detailed characterization of the films and film–substrate interfaces, and theoretical studies of the growth process.

[1] A. Y. Cho and J. R. Arthur, Progr. Solid State Chem. 10, 157 (1975).
[2] A. Y. Cho, Thin Solid Films 100, 191 (1983).
[3] M. B. Panish, Science 208, 916 (1980).
[4] K. Ploog and K. Graf, *Molecular Beam Epitaxy of III–V Compounds: A Comprehensive Bibliography 1958–1983* (Springer, Berlin, 1984).
[5] J. R. Knight, D. Effer, and P. R. Evans, Solid State Electron. 8, 178 (1965).
[6] H. M. Manasevit and W. I. Simpson, J. Electrochem. Soc. 116, 1725 (1969).
[7] For a recent review on metalorganic chemical vapor deposition, see R. D. Dupuis, in *Processing of Electronic Materials*, edited by C. G. Law, Jr. and R. Pollard (American Institute of Chemical Engineers, New York, 1987).
[8] M. B. Panish, I. Hayashi, and S. Sumski, IEEE J. Quantum Electron. 5, 210 (1969).
[9] M. Nelson, RCA Rev. 24, 603 (1963).
[10] G. B. Stringfellow, *LPE of III/V Semiconductors in Crystal Growth: A Tutorial Approach* (North-Holland, Amsterdam, 1979).
[11] T. Takagi, I. Yamada, M. Kunori, and S. Kobiyama, in Proceedings of the 2nd International Conference on Ion Sources, Vienna, 1972.
[12] I. Yamada, H. Inokawa, and T. Takagi, J. Appl. Phys. 56, 2746 (1984).
[13] I. Yamada, H. Takuoka, H. Usui, and T. Takagi, J. Vac. Sci. Technol. A 4, 722 (1986).
[14] T. Takagi, in Ref. 7, pp. 264ff and references therein.

본 연구는 과학 재단의 연구비 지원에 의해 수행 되었음.

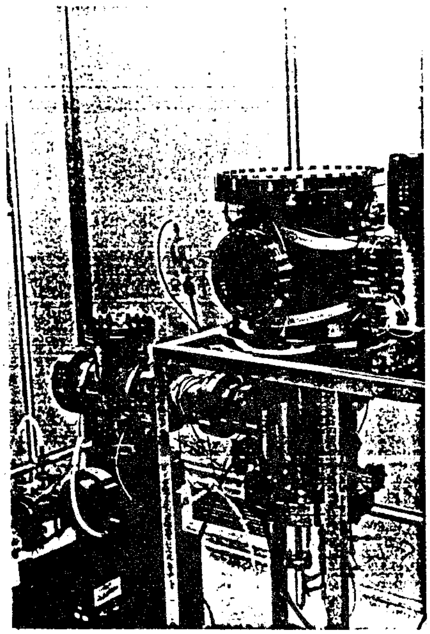

Fig.4 ICBE System

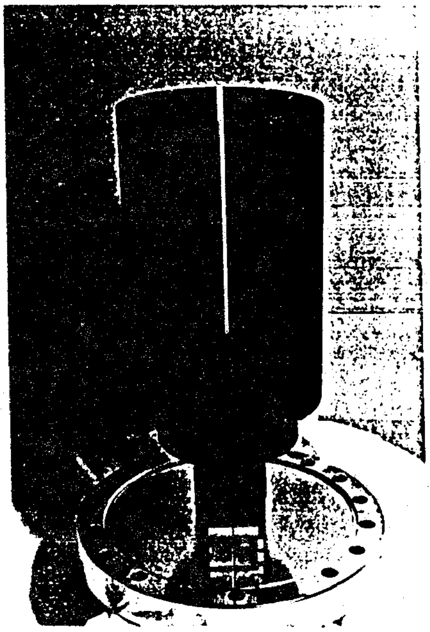

Fig.5 Heating element of crucible heater