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Preparation and structural properties of some III—V semiconductor films grown on (100) oriented Si substrates

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A laser has been used for the preparation of thin (0.01—0.5 μm) III —V/Si layers to investigate which of them can improve the growth of GaAs on a Si substrate. During the growth by this method time-resolved optical spectroscopy and Auger spectroscopy have been used to control the laser produced plasma and the composition of the film. The growth of GaAs on laser deposited GaAs/Si, InP/Si and InAs/Si intermediate layers was done by metalorganic vapour phase epitaxy (MOVPE) or by gas transport epitaxy (GTE) methods.

Structural investigation of the films has been carried out mainly by X-ray diffraction. The results show that between GaAs, InP and InAs, the GaAs films have a better quality because GaAs has the smallest lattice mismatch with respect to Si (respectively 4%, 8% and 11%). Comparing the scanning θ—2θ diagrams and the rocking curves for III—V semiconductor films grown on Si with and without laser deposited intermediate layers it can be also shown that the quality of a relatively thick (~ 1μ m) film is better in the first case.

It was shown that specially chosen laser deposited layers improve the crystalline quality of MOVPE grown GaAs films as compared to a special cutting of the Si substrate, for instance, 3° off towards Si(100) substrates.

All the results obtained give clear indications of the important role of laser deposited layers in the formation of good heterojunctions between III—V semiconductors and a Si substrate.

1. Introduction

To form an interface between two semiconductors with; different lattice parameters and/or crystal structures methods of active modification of the substrate surface are widely used. These methods are aimed to conjugate smoothly the mechanical and thermal properties of the materials as well as to overcome the creation of numerous misfit dislocations. Among these methods may be mentioned superlattice or buffer layer formation, the application of a low energy ion source of Group V elements in III—V compound growth

Laser vacuum epitaxy (LVE) is a very interesting method for this purpose because atoms and ions in a laser produced plasma effectively re-evaporate matter of the substrate and penetrate into it due to their relatively high density and kinetic energy.

This paper deals with the structural properties of the system III—V (film)—Si (substrate) grown by the LVE method in combination with gas transport reactions epitaxy (GTE) and metalorganic vapour phase epitaxy (MOVPE). LVE was used as the first stage of film growth in order to modify the substrate surface and to obtain a smooth conjugation of lattice parameters, as well as thermal and mechanic characteristics of both III—V film and Si substrate; the second stage of film growth up to a thickness typical for microelectronic application (1—2 μm) was fulfilled with the help of GTE or MOVPE.

We tried to demonstrate the importance of LVE for the formation of perfect interfaces between the materials with considerable mismatch in lattice periods, thermal and mechanical characteristics. Besides we tried to choose the composition of LVE produced intermediate layers which would give the best results at minimum thickness of the layer as well as to check the compatibility of LVE with other growth methods, especially with GTE and MOVPE.

2. Experimental procedure

2.1. Substrates

Highly polished and extra pure exactly (100) oriented and 3° off toward [011] Si(100) as well as GaAs(100) substrates from Wacker-Chemitronic GmbH, USSR micro-electronic industry and Sumimoto Electric Industries, Ltd. were used.
Si substrates were cleaned according to standard procedures of etching, washing, and drying GaAs substrates were used without any special treatment.

2.2. L VE method

The experimental set-up is shown in Fig. 1. In the chamber (1) with residual atmosphere of 10^{-8} Pa one can see the pulse laser (2) which evaporated the target (3) (2 mm thick GaAs, InP

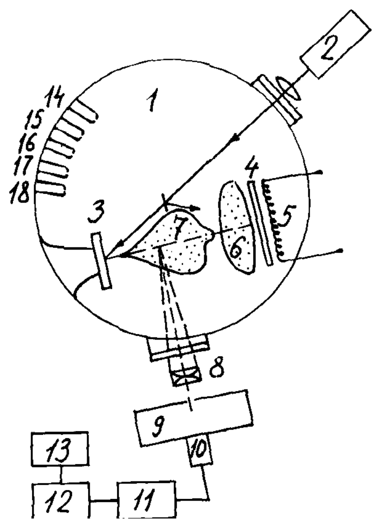

Fig.1. LVE experimental set-up.

of InAs plates), the substrate (4) heated by a thermal (5) or by a laser heater (2) (the latter heats the substrate just a few micro-seconds before a new portion of the condensate (6) from the laser produced plasma (7) of the target material enters the substrate). Depending on the type of laser (2) its characteristics are: the pulse energy 0.1—1.0 J; the pulse duration $10^{-8} – 10^{-11}$ s; the repetition frequency 10—100 Hz and the wavelength 0.337— 1.06 μm.
The plasma cluster (7) and the condensate (6) differ in composition: the first consists of only atoms and ions of the target material in a ratio of 9: 1 at a laser power density of 10^8 W/cm^2 while the latter contains both target material particles and re-evaporated substrate material particles, which are thermolised in the counter flow. The ratio between the target and the substrate particles depends on the laser power density. This ratio changes from pulse to pulse in the direction of the target material. (See also experimental results.) Monitoring of the composition, density and energy of the condensate (6) and the cluster (7) was made with the help of an optical system (8), a monochromator (9), PMT (10), boxcar-integrator (11), computer (12) and display system (13).

The standard set of diagnostic equipment inside chamber (1) includes an Auger spectrometer (14) with an argon gun (15), a mass-spectrometer (16) and low and fast energy electron diffractometers (17). With the help of the effusion cell (18) it was possible to change the ratio of the Group III to Group V element in the condensate (6).

By the described method intermediate layers (primers) on the base of GaAs, InP and InAs with a thickness of nearly 500 A were grown on the surface of Si substrates.

2.3. GTE and MOVPE methods

GTE and MOVPE were used for the growth of InP (GTE) or GaAs (MOVPE) layers directly on the substrates or on the intermediate layers grown by LVE. The GTE process was done using a standard USSR micro-electronic industry apparatus; for MOVPE the AIXTRON MOVPE 1125 system with a horizontal reactor was used.

The thickness of the layers grown by these one or two-step method was 1—2 μm as a rule.

The rule temperatures were *450* and *650°C* for GTE and *450* and *700°C* for MOVPE. Additional treatment (cleaning and annealing) of the substrate was done by heating in the reactor in H_2 (GTE) or H_2 : As (MOVPE) flow.

2.4. Investigation of the structure and properties of films

The basic methods were layer-by-layer SIMS and Auger spectroscopy as well as X-ray diffraction. A general view of the surface was obtained by optic microscopy; the luminescent characteristics of MOVPE grown GaAs films have also been investigated. Using X-ray diffraction, comparison of scanning *θ—2θ* diagrams and rocking curves for various substrates, intermediate layers, films and technological regimes it was possible to obtain the diffraction peaks of the substrate, intermediate layer and film as well as to evaluate the density of misfit dislocation from the half-width a of the rocking curve :

$$C = a^2 / 9b^2,$$

where $b = a\sqrt{2}$; *a* is the lattice period.

Using Auger and SIMS methods with layer-by-layer etching of the film we could evaluate the thickness of the intermediate layer $(III—V)_{1-x}$ - Si_{2x} as well as the continuity and the contamination of the film.

In order to compare the quality of the GaAs films grown on Si substrates the luminescence of the films excited by He—Ne laser has also been investigated.

3. Experimental results and discussion

3.1. Composition of the primers

The ion component of the target flow (mean translation energy about 100 eV) caused sputtering of the substrate and of the growing film. This sputtering effect was observed directly during condensation of GaAs on a NaCl substrate. A NaCl substrate is more convenient

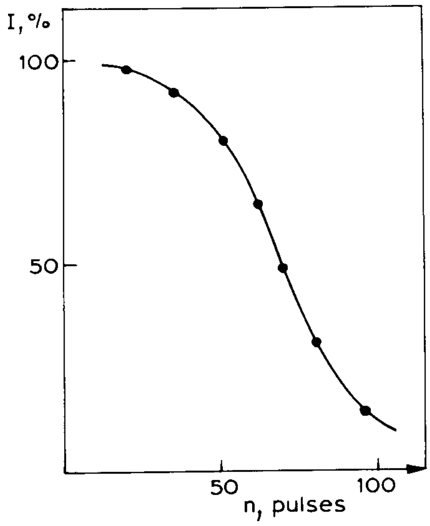

Fig. 2. 589.0 nm Na I spectral line intensity versus number of laser pulses evaporating the GaAs target. LVE growth of GaAs on a NaCl substrate.

for this kind of experiment due to the intense fluorescence of Na atoms at 589.0 nm. Fig. 2 shows the dependence of the fluorescence intensity of the 589.0 nm NaCl spectral line near the NaC1 substrate on the number of laser pulses evaporating the GaAs target. The decrease in fluorescence intensity shows that each portion of the material reevaporated from the substrate surface contains a lower quantity of substrate material than the previous one. It has been shown with the help of SIMS and Auger spectroscopy of layer-by-layer etched surfaces that in LVE grown III—V/Si structures there is a clearly determined buffer layer, the composition of which smoothly changes from the substrate material to the target evaporated III—V semiconductor (see, for instance, fig. 3). Depending on the growth conditions an appreciable concentration of Si is registered by these methods within the 0.02—0.10 μm limits. It should be noted that the ion action has bilateral character. The ion component in the laser produced plasma not only sputters the substrate material which intermixes with the flow of target components in the transitional region and then precipitates again on the substrate, but also leads to an intense generation of point defects near the substrate surface and, as a result, to the

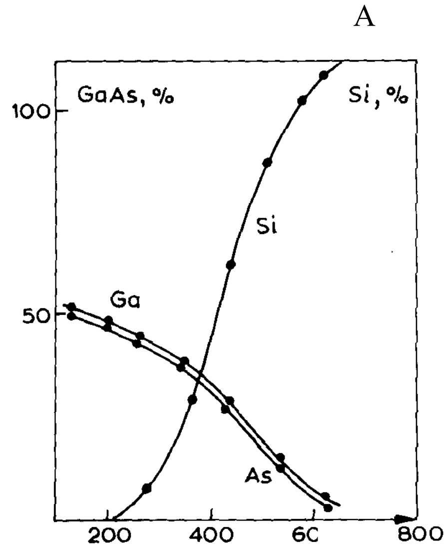

Fig. 3. Distribution of Ga, As and Si concentration inside the LVE intermediate layer according to Auger spectroscopy measurements.

formation of a metastable solid solutions. Obviously, in the case of III—V/Si structures there is a $(III—V)_{1-x}$ —Si_{2x} solid solution with x varying from 1 to 0.

3.2. Quality of the films grown by MOVPE or GTE depending on the type of L VE primers

Only the GaAs films grown on GaAs substrates were single crystals, while the films grown on Si had a textured structure and, in some cases, were very close to a single crystal.

The results of X-ray diffraction investigations show that among the GaAs, lnP and InAs thin (—' 500 A) films grown by the LVE method (actually the films were III—V/Si solid solutions) the GaAs films had a better quality because of the smaller lattice mismatch with respect to Si (respectively 4%, 8% and 11%). Typical rocking curves for GaAs and InP are shown in fig. 4a. One can see that the half-width of the peaks for InP is nearly 7 times greater that for GaAs.

Now let us compare the results obtained with and without the LVE grown primers of various III—V compounds for GTE and MOVPE.

For the GTE method we see from fig. 4b that the quality of the InP film grown on a $(InP)_{1-x}$—Si_{2x} primer was better than the quality of the InP film grown by the usual two-step technology (step 1: *450°C;* step II: *650°C).* Similar results can be seen in the case of MOVPE of GaAs (fig. 4c). Based on the above mentioned results we tried to choose the better primer for MOVPE of GaAs film growth. From fig. 4b. one can see that the most perfect GaAs films were grown with the help of the primer on the base of a $(InAs)_{1-x}$—Si_{2x} non-equilibrium solid solution. Obviously, in spite of the great mismatch in the lattice parameters between InAs and Si(11%) we can easily reach with a rather thin primer the necessary conjugation in the lattice periods, and mechanical and thermal properties using for GaAs film growth a $(InAs)_{1-x}$—Si_{2x} primer instead of pure Si or even a $(GaAs)_{1-x}$—Si_{2x} primer. It should be noted that the half-width of the peak on the rocking curve for GaAs grown on $(InAs)_{1-x}$—Si_{2x} and exact Si(100) is only a few tenths of a degree which is close to the results known from the literature for GaAs films grown 3° off toward Si(100) substrates and nearly 10 times less than that for thin LVE grown a $(GaAs)_1$-x—Si_{2x} primer.

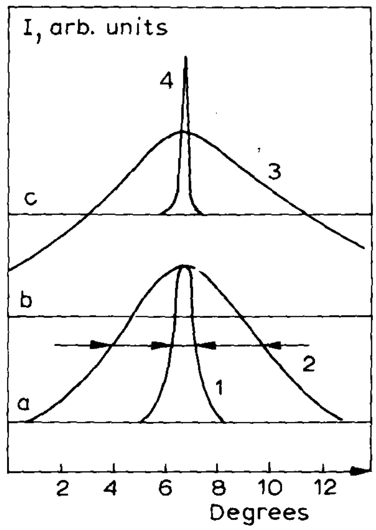

Fig. 4. X-ray diffraction. Rocking curves. (1) 500 A LVE intermediate layer on the base of GaAs as grown on a Si substrate. (2) InP film grown on a Si substrate with a LVE intermediate layer on the base of lnP. (3) InP film grown directly on a Si substrate. (4) GaAs film grown on an $InAs)_{1-x}$—Si_{2x} intermediate layer.

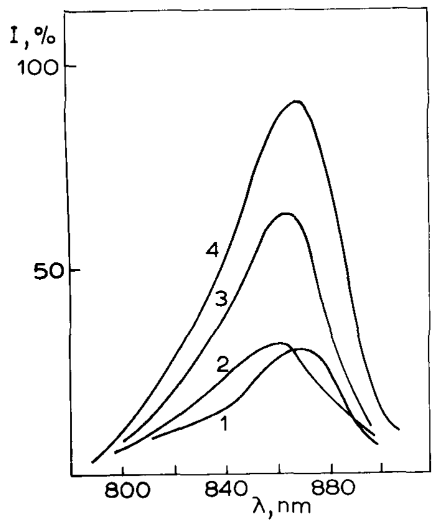

Fig. 5. Luminescence of GaAs film at room temperature. (1) LVE intermediate layer on the base of GaAs; exactly (100) oriented Si substrate. (2) GaAs film grown directly on exactly (100) oriented Si substrate. (3) GaAs film grown on $(InAs)_{1\sim}$—$Si_{2\sim}$ primer; exactly (100) oriented Si substrate. (4) GaAs film grown on 3° off toward Si(100) substrate.

Thus, we can see that the application of $(InAs)_{1-x}$—Si_{2x} could prevent the formation and propagation of dislocations into active device structures on the base of GaAs. Evaluation of the misfit dislocation density gives a value of nearly 10^7 cm^{-2}, of course, this is a rather high value, but we hope that it may be improved in future.

MOVPE grown GaAs films on various substrates and primers were independently compared by X-ray diffraction, SIMS, Auger spectroscopy and luminescence investigations. It was shown that a specially chosen LVE primer leads to the same or even a better quality of MOVPE grown GaAs films than a special cutting of the Si substrate, for instance, 3° off toward substrates instead of exact (100) oriented Si. For instance, such a conclusion could be made by comparing the shape and the intensity of the luminescence spectra in Fig. 5 despite of some inaccuracy in the luminescence method.

4. Conclusion

All the results give clear indications of the important role of laser deposited intermediate layers in the formation of interfaces between III—V compounds and Si. Of course, the application of LVE primers can be effective only in case of good performance of all stages of the substrate treatment and the actual growth process.

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References

[1] J. Green, S. Barnett and A. Rockett, AppI. Surf. Sci. 22/23 (1985) 520.

[2] S.L. Pyshkin, S.A. Fedoseev, S.N. Chechuy and V.1. Shudlov, in: Proc. Optika '80, mt. Symp. on Modern Optics, Lectures, Budapest, Vol. 11(1980) p. 488.

[3] V.A. Budyanu, SN. Chechuy, l.A. Damaskin, S.A. Fedoseev, A.A. Nasakin, S.L. Pyshkin, M.I. Valkovskaya and V.P. Zenchenko, Phys. Status Solidi (a) 91(1985)152.

[4] V.A. Budyanu, S.N. Chechuy, IA. Damaskin, S.A. Fedoseev, A.A. Nasakin, S.L. Pyshkin, MI. Valkovskaya and V.P. Zenchenko, Rev. Roum. Phys. 32 (1987) 215.

[5] R.J. Matyi, J.W. Lee and H.F. Schaake, J. Electron. Mater. 17 (1988) 87.

[6] V.P. Zenchenko, V.P. Zenchenko, S.L. Pyshkin, S.A. Fedoseev and V.A. Budyanu, in: Proc. Optika '88, mt. Symp. on Modern Optics, Budapest, Vol. 11(1988) 473.

[7] H.-S. Kim, Y. Kim, M.-S. Kim and S.-K. Mm, J. Cryst. Growth 92 (1988) 507.