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LASER 光勵起 氣相反應에 의한 Ⅲ-Ⅴ 族系 光電材料의 Hetero-Epitaxy 考察

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LASER-Induced Vapour Phase Hetero-Epitaxy of $A^{III}B^{V}$ Type Opto-Electronics

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요 약

본 연구에서는 고밀도 광원 활용에 의한 유기금속화합물의 광분해 반응을 이용하여 $A^{III}B^{V}$ 형 광전재료의 Hetero-epitaxy를 고찰하였다.

실제로 ArF Excimer laser(파장 193nm)에 의하여 Ⅲ족원으로 trimethylgallium과 Ⅴ족원으로 Ammonia의 2분자간 광분해 반응을 이용, (001)면 Sapphire 기판상에 증착시켰다. 생성되는 성막상태는 주사식 전자현미경, X-ray 회절 및 전자선 회절법(RED)에 의하여 평가하였다. Laser 光勵起 유무에 따라 결정병합 상태 및 결정형태에 현저한 차이를 관찰할 수 있었으며, 특히 결정격자의 방위성에 큰 영향을 주고 있음이 주목되었다. 광원 조사방법은 수직조사에 의한 기판면 여기보다는 수평조사에 의한 기상 반응물 여기가 더 효과적이였다.

Laser 광여기에 의한 성막층의 격자형성은 다음과 같은 2가지 Model중 하나로 설명 할 수 있었다.

(001)면 Sapphire // Wurzite형 GaN의 (001)면

또는

(001)면 Sapphire // Wurzite형 GaN의 (001)면 → Twinned Zincblende형의 GaN(111)면

Abstract

The hetero-epitaxial growth of $A^{III}B^{V}$ type opto-electronic material is attempted by means of the laser-induced chemical vapour deposition technique. The bimolecular gas phase reaction of trimethylgallium with ammonia on (001) alumina substrate for the epitaxy of gallium nitride is chosen as a model system. In this study, ArF excimer laser (193nm) is employed as a photon source.

Marked difference is found in nucleation and in subsequent crystal incorporation between the deposits formed with and without the laser-irradiation. The surface coverage with isomorphically grown crystallites is pronounced upon "volume-excited" irradiation in comparison with the conventional thermal process.

As to the crystal structure of the grown layers, the laser-induced deposits of GaN may be represented by either of the following two models:

(001) plane of sapphire // (001) plane of wurtzite-type GaN,

OR

(001) plane of sapphire // (001) plane of wurtzite-type GaN

↓

(111) plane of twinned zinc blende-type GaN

INTRODUCTION

Gallium nitride (GaN) is one of the most promising opto-electronic materials and attracts much interests in recent years. Because of its direct band-gap energy(Eg) of 3.504 eV at an ambient temperature [1], important applications are envisaged for the emission of light in the regions from the visible to the ultra-violet wavelengths.

Undoped GaN is n-type semiconducting material with electron concentrations of $\geq 10^{17} cm^{-3}$ [2,3]. The dominant donor is believed to be the nitrogen vacancy.

The epitaxial growth of GaN has been studied with moderate success from the use of trimethylgallium (TMG) as a gallium source and ammonia or hydrazine as a nitrogen source by metal-organic chemical vapour deposition(MOCVD) techniques [4].

Due to the pyrophoric nature of hetero-epitaxial constituent(s), lattice mismatches and inclined dislocations are serious problems in all the existing thermal processes. It would be a meaningful approach that the growth of gallium nitride may be carried out at lower temperatures in order to decrease the concentration of thermodynamic defects such as nitrogen vacancies occurring at elevated temperatures [5].

The laser-aided CVD techniques have been well advanced particularly for hetero-epitaxy at lower temperatures.

In this study, the characteristic behaviours of the GaN deposition on c-faced alumina substrate are investigated under an ArF excimer laser source with an ultimate aim of defect-free GaN photo-epitaxy.

EXPERIMENT

Fig. 1 Shows a typical scheme of the laser-induced deposition chamber in use.

In laminar irradiation, the focused laser beam is guided to follow the parallel path, 10㎜ above the substrate surface.

Basal sapphire wafers(c-face single crystals) are used as substrate. For measurement of substrate temperature, an optical pyrometer is used with calibration. Before the reactant feed, the chamber is evacuated down to the vacuum strength of not less than $2x10^{-6}$ torr.

Upon reach of this vacuum level, high-purity NH_3 gas at the flow rate of 300 sccm is admitted. When the substrate is stabilized to a deposition temperature within ±5℃ at typically 900℃, the laser irradiation starts with flow of trimethylgallium at a rate of 5 sccm. The TMG in use is of ultra-pure(6N) grade and cylinder-chilled to 0℃ prior to use.

Both of the reactant gases are allowed to be well mixed and preheated to about 400℃ immediately before the entrance of the reaction chamber. Throughout the deposition experiment, the total pressure of the reacting chamber is kept constant, typically at 0.17 torr. The photon source in use is an ArF excimer laser (ex. Lambda Physik EMG 103 MSC) of 193 nm. The laser has pulse duration of 17 ns and is operated at repetition rates up to 150 Hz with microprocessor control. For the surface-parallel(or laminar) irradiation, the laser beam of 25.9mJ per pulse is used. The focused beam is permitted to pass through a quartz window along the laminar path about 10㎜ above the substrate surface.

Alternatively, the substrate surface is co-irradiated perpendicularly by the laser beam(reflected) of 4.1mJ per pulse. All the photo-deposition results are observed as a function of reactant flow-time at a fixed deposition temperature.

The growth rate is estimated from the variations of

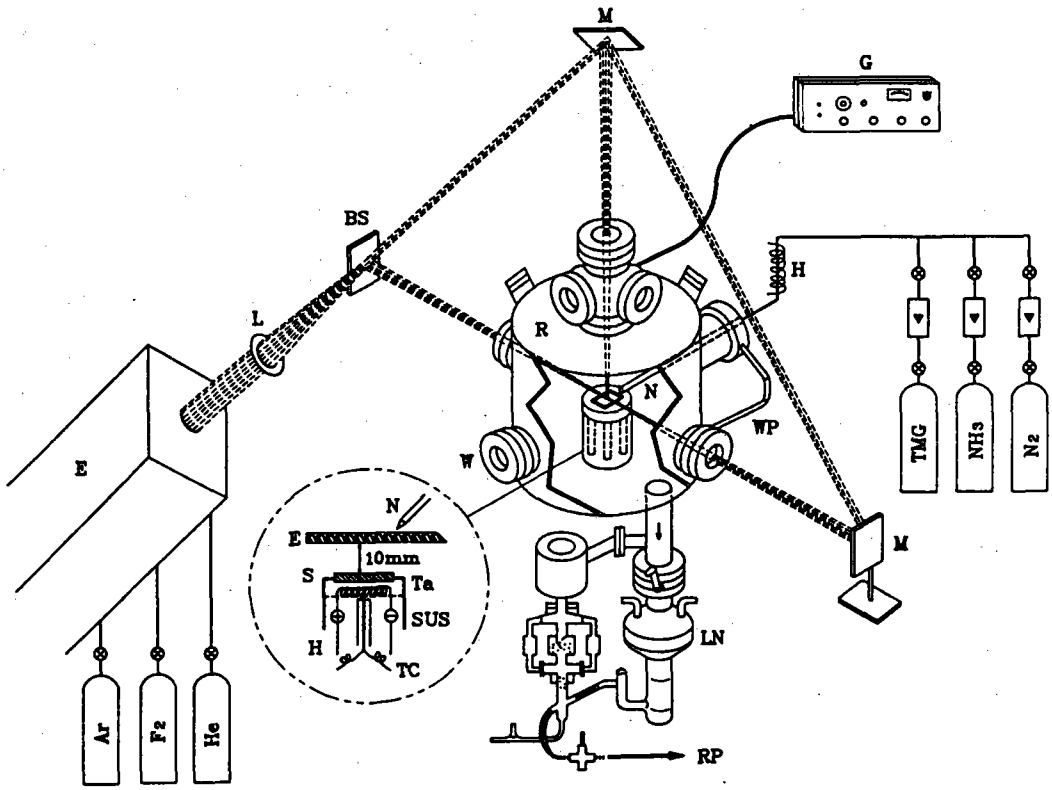

Fig. 1 Scheme of Experimental Apparatus for LCVD of GaN on (001) Alumina Surface
– Parallel / Perpendicular Photon Flux Depicted –

B S=Beam Splitter	T a=Tantalum Heating Coil	H=Heating Coil	R=Deposition Reactor
D P=Diffusion Pump	T C=Thermocouple Wire	L=Lens	R P=Rotary Pump
E=ArF Excimer Laser Beam	T M G=Trimethyl-gallium	L N=Liquid Nitrogen Trap	S=Substrate Wafer
F=Filter	W=Quartz Window	M=Dielectric Mirror	S U S=Metal Susceptor
G = Vacuum Gauge / Power Monitor	W P=Window Purge	N=Gas In-let Nozzle	

the crystallite dimensions with deposition time.

The crystalline nature and the surface morphology of GaN deposits are characterized by means of X-ray diffraction(XRD), reflection electron diffraction(RED) and scanning electron microscopy(SEM), respectively.

RESULTS AND DISCUSSION

Typical SEM microphotograms of GaN deposits are shown in Fig.2, while the changes in growth as observed with variation of the deposition time are given in Fig.3.

They indicate that the deposition begins with sporadic formation of fine particulates, the adherent being SEM-detectable from the specimens of 10-min's laser-deposition.

From the GaN deposition through the thermal process, it is postulated that the TMG molecules may lose their methyl radicals progressively [6-8]

It is also stated that with the laser beam of 193 nm, the molecules may undergo complete decomposition up to the state of neutral atomic gallium.

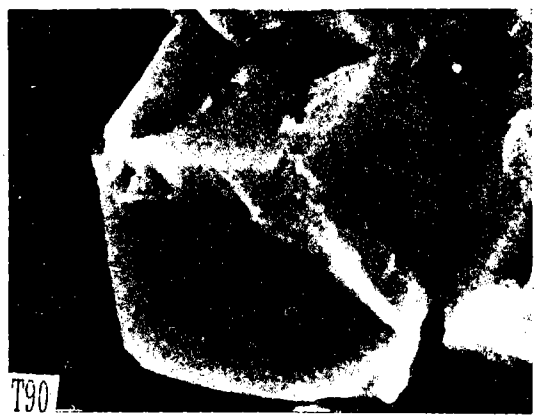

Fig. 2 Sem photo – micrograph of laser – induced GaN deposits on (0001) sapphire substrate
Max growth among observations
scale 2 μm
Deposition time in min indicated, L=Laminar, S=Substrate & s=Tilted.

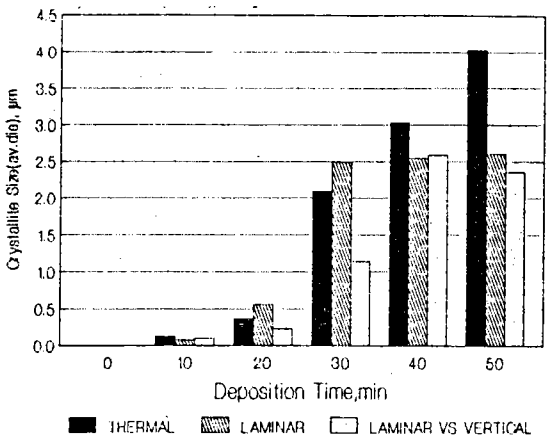

Fig. 3 Plots of Crystallite Size vs Deposition Time, as Observed from SEM Photomicrograph of Typical GaN Deposits with and without Laser Irradiation.

On the other hand the ammonia molecules will be dissociated into amidogen(NH) radicals and hydrogen(H) atoms under the analogous condition. The laser-fragmented surface reactions may be postulated as follows (loc.cit.):

$$\underset{\text{unstable}}{Ga(CH_3)_3} \xrightarrow{-CH_3^{\cdot},\triangle} \gg Ga(CH_3)_2 \xrightarrow[\text{stable}]{-CH_3^{\cdot}} \gg$$

$$GaCH_3 \xrightarrow{-CH_3^{\cdot},\triangle+h\nu} Ga$$

$$NH \xrightarrow{-H\cdot,\triangle+h\nu} NH_2 \xrightarrow[\text{reactive}]{-H\cdot} \gg NH$$

$$Ga(CH_3)_3+NH_3 \xrightarrow{h\nu} \gg (CH_3)_3\,Ga{:}NH_3 \xrightarrow[\text{monoammoniate adduct}]{-CH_3^{\cdot},-H\cdot} \gg GaN(g)$$

$$GaCH_3+NH_3+SITE \xrightarrow{-CH_4,h\nu} GaN\text{–}SITE$$

$$Ga+NH_2+SITE \xrightarrow{-H_2,h\nu} Ga\text{–}SITE$$

$$GaN(g)+SITE \xrightarrow{\triangle} GaN\text{–}SITE$$

NOTE : (.)Free Radical,(⇒) Reaction Easy, (→) Reaction Difficult

As to the crystalline nature of the laser-induecd GaN deposits, SEM morphological assessments and RED patterns of lattice structures are discussed.

The SEM micrographs reveal that in the initial depositions of $\leq$30 min, most of the surface-dangled particulates are overwhelmingly hexagonal in shape. In the later stages of the growth, these particles are turned out to grow into pyramidal-shape crystals, as

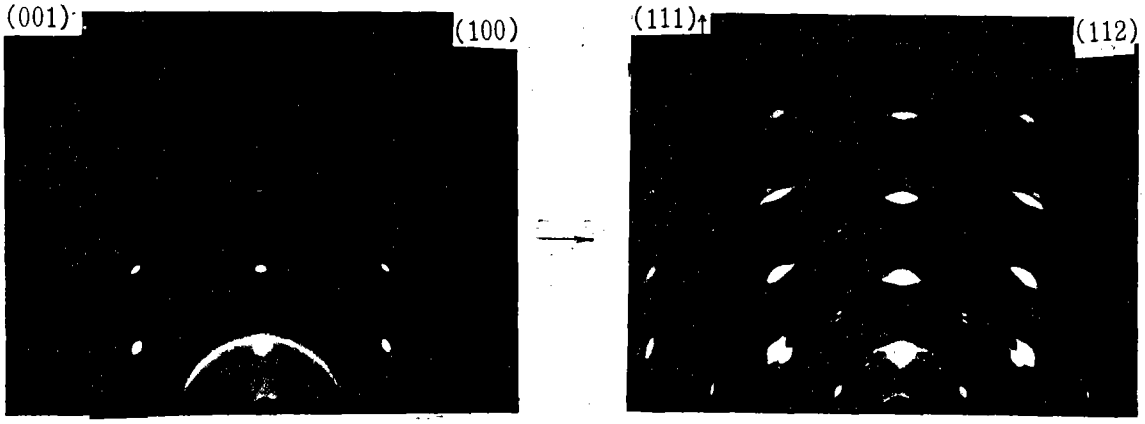

Fig. 4 Typical RED Patterns of Laser-induced GaN Deposits

evidenced from the tilted view of the specimens(Fig 2). From the thermal and/or some prolonged laser deposition process(es), formation of prism-like crystals is manifested in scattered deposits (T90 of Fig 2). It must be remembered that the hexagonal plate can be seen only from the laser-assisted deposits. In the thermal process, there is no evidence for hexagonal crystallites from any of the specimens, irrespective of the deposition times allowed.

Typical RED(Reflection Electron Diffraction) patterns of the laser-induced GaN deposits are shown in Fig 4.

The pyramidal deposition of GaN in the wurtzite type takes place in such a manner that the (001) plane may grow with orientation in parallel to the (001) face of the sapphire substrate, viz.

(001) plane of sapphire // (001)GaN ad-layer of wurtzite-type

In contrast, the GaN deposition in a zinc blende type will occur in relatively complex manner, presumably through the formation of the cubic crystallites via twin introduction.

The stacking fault of the wurtzite structure may be interfaced along the (111) direction of zinc blende type crystal, the basal plane being assigned to (001) face.

The occurrence of the zinc blende type deposits may be represented by the model:

(001) plane of sapphire // (001) GaN ad-layer of wurtzite type

↓

(111) plane of GaN ad-layer of twinned zinc blende type

It appears that RED evidence is in support of this interpretation.

From the above discussions the following highlights may be drawn to attention.

1. The laser-induced deposition of GaN on the sapphire single crystal begins with the spotty nucleation, the nuclei of uniform sizes being densely populated over the surfaces, which occurs more effectively than those from the thermal process.
2. By the laminar irradiation the growth of the nuclei is rapidly enhanced up to the deposition time of, say$\lesssim$30 min since commencement, but the growth virtually ceases with the extended depositions beyond 40 min(Fig 3).
3. Similar effects are found from the crystal growth under surface co-irradiation, but less uniform and reduced, when compared to the case of laminar irradiation alone.
4. The surface appendages of GaN formed from the laser irradiation are observed initially as hex-

agonal thin plates, which grow into pyramidal structure of wurtzite type(L30s, Fig.2). Upon prolonged laser-deposition or thermal deposition, however, the surface ad-layers predominantly take a prism shape, which may grow into zinc blende type GaN(T90, Fig.2).

5. The GaN deposits from the 40-min's laminar irradiation are found as smooth and rounded conglomerates, which are composed of the original crystallites locally grown and fused into the substrate structure(LS40s of Fig 2). The microscopic appearance of the ad-layered surface is unlikely to be flattened as a whole.

CONCLUSIONS

From the evidence it may be concluded that the laser-induced chemical vapour deposition of GaN on(001) sapphire confers higher density of nuclei population and occurs at temperatures lower than those of the conventional thermal process.

The hexagonal plates are formed as initial layers of the deposits, which lead to the epitaxial growth of GaN in wurtzite type structure.

The growth rate tends to decrease with increase in deposition time, probably due to the photo-deposition of the adsorbed species. All the outstanding results are attributed to the effects of laser fluence, being involved with selective interaction of photolytic radical species with the surface sites.

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