# In Situ Distinction of As-Rich Initial Surfaces by Millisecond Time-Resolved Reflectance Difference

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The fast evolutions of As dimer density and Ga dimer density were measured by using a millisecond time-resolved reflectance difference (RD) system during the short-pulse supersonic nozzle beam epitaxy (SSBE) growth of GaAs on Asrich initial surfaces. Under the impingement of trimethylgallium (TMGa) short pulse, the  $(2x4)\beta$ ,  $(2x4)\gamma$ , and c(4x4) initial reconstructed surfaces showed distinguishable transient RD signals because these As-rich surfaces have different bond structures result in unlike reaction kinetics.

## 1. Introduction

During the epitaxial growth of compound semiconductors, the initial surface reconstruction of the substrate also must be selected carefully because of its great control on the quality of interface. It is probably due to that the different reconstruction of surface has different dominating kinds of dimers resulting in different surface bond structure. Different reconstruction has different growth behavior and must be distinguished very clearly during the growth process for further understanding the epitaxial growth mechanisms. It has been understood that there are mainly two kinds of As dimers and one kind of Ga dimers on (001) GaAs reconstructed surfaces in ultrahigh vacuum (UHV) as well as in atmospheric pressure (AP).1) Measuring the relative surface coverage of Ga2) and As dimers in real time during the epitaxial growth can provide new insight in the growth mechanism and surface reaction kinetics, because the dimer annihilation and formation are playing important roles in the growth. This is very important for the short-pulse supersonic nozzle beam epitaxy (SSBE)3) and related epitaxy techniques, because the organometallic source molecules decomposition process strongly depends on the surface bonds.4)

By combining a millisecond time-resolved reflectance difference<sup>5)</sup> system with SSBE, we measured the evolutions of As dimer and Ga dimer density in real time during the epitaxial growth of GaAs on  $(2x4)\beta$ ,  $(2x4)\gamma$ , and c(4x4)initial surfaces. Different initial reconstruction shows different dimer density evolution behavior and can be distinguished in some hundreds of milliseconds by the kinetic acquisition of RD signal during the epitaxy.

## 2. Experiment procedure

The experiments were performed in an SSBE system, using cracked AsH, (100%) and TMGa as arsenic and gallium sources, respectively, for detail, see references 3, 5, and 6. By changing the flow rate of arsine that was being continuously supplied during the experiments, different initial reconstructions had been obtained which can be simultaneously determined by reflectance different spectroscopy (RDS) and reflectance high energy electron different (RHEED), they also can be identified with each other by real time kinetic acquisition of RD signal as described later. The RD data  $\Delta r/r = 2 \text{Re}[(r_{110} - r_{110})]/[(r_{110} + r_{110})]$ , where  $r_{110}$  and  $r_{110}$ are near-normal incidence complex reflectances for light linearly polarized along [110] and [110], respectively, were obtained by using a RD set-up,5) the RD signals at 2.6 eV and 1.9 eV were recorded, which respond to the evolutions of As dimer density and Ga dimer density under the TMGa short pulse impingement, respectively.

## 3. Results and discussion

Fig. 1 shows the transient RD signals at 2.6 eV responding to the evolutions of As dimer density when  $(2x4)\beta$ ,  $(2x4)\gamma$ , and c(4x4) initial surfaces were exposed to a TMGa short pulse supersonic nozzle beam. The TMGa short pulse was started at the time of zero. For  $(2x4)\beta$  initial surface, the RD signal intensity decreased as soon as the TMGa short pulse was started, and the reconstruction changed into Ga-rich. After the TMGa short pulse was stopped, the RD signal rose to the same intensity value as that of the beginning point. While for  $(2x4)\gamma$  and c(4x4), the RD signals



Fig. 1. Transient RD signals on (a)  $(2x4)\beta$ , (b)  $(2x4)\gamma$ , and (c) c(4x4) reconstructed initial surfaces upon the injection of TMGa short pulse supersonic nozzle beam.

increased to their first maximum points (where the reconstructions showed  $(2x4)\beta$ ) and then decreased. When TMGa short pulse was stopped, the RD signals increased to their second maximum intensity values (where the reconstructions also showed  $(2x4)\beta$ ) and then recovered. The RD signal evolutions on these three kinds of As-rich initial surfaces show quite different beginning points and unlike evolving behaviors with different time constants, these distinguishable RD signal evolutions give us an opportunity to identify the As-rich initial surfaces in real time.

The surface reconstruction of the  $(2\times4)\beta$  has been confirmed that there are three As dimers along [ $\overline{1}10$ ] and one missing dimer in one unit cell. The  $(2\times4)\gamma$  surface has been proposed <sup>7</sup> that there have two As dimers in one unit cell, one is along [ $\overline{1}10$ ] direction and other one is along [110] which we called "excess top layer As dimer". It has been observed that the outermost layer of the  $c(4\times4)$  reconstruction consists of three As dimers parallel to [110].<sup>8)</sup>

When the TMGa short pulse impinged on  $(2x4)\beta$  initial surface, the bonds of As dimers along [ $\overline{1}10$ ] were broken as the result of the decomposition of TMGa molecules, this As dimer annihilation process made the initial great decrease in RD signal at 2.6 eV. In company with the As dimer annihilation process, Ga dimers along [110] direction formed on As atoms, this Ga dimer formation made RD signal at 1.9 eV decreased as shown in Fig. 2. No delay have been measured in RD signal at 1.9 eV, this fact revealed that at this high



Fig. 2. Transient RD signals on  $(2x 4)\beta$  initial surface. The annihilation of the As dimers along [ $\overline{110}$ ] in company with the Ga dimer formation along [110] proceeded in the initial stage.

temperature, the decomposition process of TMGa on  $(2x4)\beta$  proceeded too fast. When this Ga dimer formation process finished, the surface reconstruction evolved into Garich surface and saturated until the TMGa short pulse was terminated. From this time point, the surface began to evolve into the  $(2x4)\beta$  surface due to that the Ga dimers along [110] were broken by As dimer formation along [110].

For  $(2x4)\gamma$  initial surface, the great increase in RD signal at 2.6 eV at the initial stage can be seen in Fig. 1(b). The excess top layer As dimer along [110] on the  $(2x4)\gamma$  surface was annihilated while the four underlying As atoms formed two As dimers along [110] because of TMGa molecules decomposition and dissociation. The surface reconstruction changed from  $(2x4)\gamma$  into  $(2x4)\beta$ , we called it transient  $(2x4)\beta$ . This transient  $(2x4)\beta$  surface had a lower RD signal intensity than that of the  $(2x4)\beta$  initial surface because there were adsorbed TMGa and decomposition products on the surface, the coupling between the detect light and the dimer bond would be reduced by the adsorption of the TMGa on the bond. The detail transient RD measurements on  $(2x4)\gamma$  initial surface can been seen in reference 9.

The c(4x4) initial reconstruction also changed into transient  $(2x4)\beta$  under the impingement of TMGa molecules. The increase in RD signal at 2.6 eV from the minus start point in intensity to the first maximum point was due to the desorption of the outmost layer As dimers along [110] and the As dimer formation along [110] of the second As



Fig. 3. As dimer density evolutions on c(4x 4) initial surface with different TMGa source pressures.

layer atoms, the surface evolved into transient  $(2x4)\beta$  surface. The period that the As dimer annihilation along [110] and the As dimer formation along [110] in the initial stage of transient RD signal was reduced by increasing the TMGa source pressure, that was, the supply rate of TMGa in our experiment. The results can be seen in Fig. 3. After the surface evolved into transient  $(2x4)\beta$ , Ga dimers formed along [110] resulted in the annihilation of the As dimers along [110], the surface changed into a Ga-rich reconstruction which was identified at the valley of RD signal.

Our RD signals show that the  $(2x4)\gamma$  and the c(4x4)As-rich surfaces evolved into  $(2x4)\beta$  surface usualy when they were exposed to the TMGa short pulse, the As dimers along [110] formed upon other As atoms were annihilated easily by the decomposition of TMGa. The  $(2x4)\beta$  reconstruction also showed up when the specific environment was changed by, for example, the TMGa short pulse impingement termination. This means that the  $(2x4)\beta$  surface would has great both steric and electronic stabilities than other As-rich reconstructions even in the growth process. The  $(2x4)\beta$  surface would be the most active surface when it was exposed to TMGa, because the Ga dimers only formed on  $(2x4)\beta$  reconstructed surface rather than on  $(2x4)\gamma$  or c(4x4).

# 4. Conclusions

We have measured the fast evolutions of As dimer and Ga dimer density in real time during SSBE growth of GaAs on As-rich initial surfaces by using a millisecond time-resolved RD. Under the injection of TMGa short pulse, the  $(2x4)\beta$ ,  $(2x4)\gamma$  and c(4x4) initial surfaces show distinguishable transient RD signal evolutions because these As-rich surfaces have different bond structures.

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