Effect of reactive ion beam etching on the photoluminescence of CdTe epitaxial layers

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We demonstrated the effect of reactive ion beam etching (RIBE) process on the PL properties of CdTe/sapphire metal organic vapor phase epitaxy layers. At optimum conditions, the RIBE attack does not make significant morphological changes but it results in an increase of the concentration of acceptor impurities. This was revealed by an increase of the overall photoluminescence (PL) intensity and, simultaneously, a decrease of the PL decay time, more important on the low energy side of PL spectrum due to the recombination of carriers in acceptor pairs. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2874480]

During recent years, there has been essential progress in epitaxial growth of CdTe epilayers on different substrates such as Si, GaAs, or sapphire by metal organic vapor phase epitaxy (MOVPE), given the current and potential applications of this material for infrared optics and electronics, photonics, radiation detectors, etc. (Refs. 1 and 2 and references therein). As an important advantage compared to other semiconductors such as Si or III-V's, it was shown that the epitaxial growth of CdTe is possible on substrates either having very different lattice constants or even amorphous structure due to the high plasticity of CdTe.[3] Besides the lattice mismatch, the layer quality also depends significantly on the particular growth conditions, making difficult the comparison of different previous results.[4,5] In spite of these problems, reasonable optical and structural quality can be obtained in CdTe epilayers grown onto sapphire substrates, even if the accumulated stress on the interface can produce an important surface roughness.[6–8]

For technological applications of CdTe epilayers, it is necessary to develop several processes that affect their surfaces, particularly reactive ion beam etching (RIBE). This process is a typical one to produce pixels and photonic bandgap structures onto semiconductors and other particular photonic and optoelectronic devices.[9] In the present paper, we study the effect of the RIBE process on the photoluminescence (PL) of CdTe epitaxial layers grown on sapphire by MOVPE.

CdTe single-crystalline layers were grown in a low-pressure horizontal MOVPE reactor under optimal growth conditions.[6,7] Dimethyl cadmium and di-isopropil tellurium were used as precursors, the growth temperature was 340 °C, and the growth time was in the range of 2–4 h. A commercial substrate of sapphire misoriented 3° off the (0001)-plane was used to obtain CdTe epilayers orientated along the (111)-direction. The thickness of the layers used in this work was in the range of 5–7 μm.

The as-grown CdTe epilayers were divided into several areas by optical lithography using a Karl–Süss MJB3 mask aligner and some of these areas were protected with a 0.3 μm thick layer of aluminium evaporated over the photoresist. After that, a RIBE attack was performed on these samples using a RIB-ETCH reactor. The RIBE process was carried out under $(CH_4+H_2)/N_2$ plasma atmosphere for 90 min. The ion energy was 400 eV and the total reduction of epilayer thickness was about 1.5 μm.

The morphological characterization was carried out by an atomic force microscopy (AFM) (Nanotec). The continuous wave (cw) PL experiments were performed by using a doubled Nd:YVO_4 (Verdi) pumped Ti:sapphire laser (Mira 900D) as excitation source. Multichannel detection of the PL spectra was performed with a 0.3 m focal length double spectrograph and a back illuminated cooled Si charge-coupled device (Andor). For time resolved PL (TRPL) experiments, the same Ti:sapphire laser was used under passively mode-locked operation. The PL signal was dispersed by a single 0.5 m focal length imaging spectrograph and detected by a synchroscan streak camera (Hamamatsu C5680) with a type S1 cooled photocathode.

Figure 1 presents typical images of the CdTe epilayer

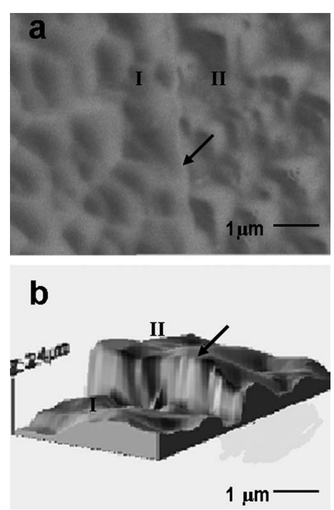

FIG. 1. Surface microrelief of CdTe epilayer recorded by optical (a) and AFM (b) microscope after the RIBE process: (I) etched area and (II) protected area with the as-grown morphology and arrow indicates the boundary between both areas.

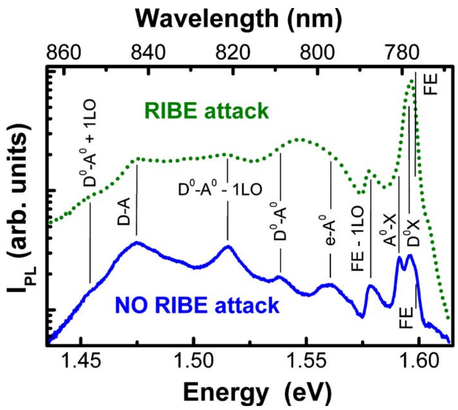

FIG. 2. (Color online) PL spectra at 10 K under near resonant conditions (710 nm) and low excitation power in zones of the CdTe surfaces with (dotted line) and without (continuous line) RIBE attack. The difference in intensity is that really measured between both zones.

surface after the RIBE process and removal of the photoresist protecting the original surface. It is observed that the etched (I) and as-grown (II) areas have a similar microrelief with an average roughness of 400 nm. We only detect a weak increase by about a 10% in the CdTe zones that were exposed to the RIBE attack. This demonstrates that the RIBE process under optimum technological conditions does not introduce noticeable morphology modifications of the exposed surfaces with respect to that observed in the as-grown case.

Figure 2 shows a typical PL spectrum at 10 K under near resonant conditions in the zones of CdTe layer where RIBE was practised, as compared to that obtained in the zones protected against it. The assignation of the different recombination features in the zones without RIBE, where more lines can be resolved, is indicated in Fig. 2 on the basis of previous studies in similar CdTe samples.[2,4,7] In these zones, the high energy part is the sum of several excitonic contributions, particularly three lines narrower than 3 meV peaked at 1.591, 1.5955, and 1.598 eV, which are associated with acceptor bound-exciton (A°X), donor bound-exciton (D°X), and near free-exciton (FE) recombination, respectively.[2,4,7,10,11] A high energy shoulder less intense than exciton related recombination lines is detected at around 1.606 eV, which can be attributed to free carrier recombination and even above barrier donor-related recombination due to phonon absorption.[12] The observation of this kind of recombination lines is indicative of a reasonably good optical quality of the as-grown CdTe epilayers. The broader line peaked at around 1.579 eV can be attributed to the 1-LO phonon replica of the FE recombination. The band at 1.560 eV is due to free electron-acceptor (eA°) recombination, whose corresponding phonon replica can be close to the energy of the neutral donor-acceptor (D°A°) transition, giving rise to the observed band peaked at around 1.537 eV.[7] The intense resonance at 1.515 eV can be attributed to the first phonon replica of the D°A° transition, and the weaker contribution at around 1.493 eV (deconvoluted at the low energy part of the PL spectrum) to a second phonon replica. The most intense PL band at 1.475 eV, together with a low energy PL shoulder, are associated with the carrier recombination through donor-acceptor pairs (DAPs) and its corresponding 1-LO phonon replica. These pairs can be due to the group I residual impurities and their complexes with cadmium vacancies, which are common in bulk and epitaxial layers of CdTe.[1–8,13,14]

All the recombination features described above are common for both types of zones at the CdTe surface, with and without RIBE attack. The main differences are the emission intensity and the better definition of the PL resonances in the zones without RIBE attack. The integrated intensity in the spectral regions of 1.435–1.540 eV (neutral and pair donor-acceptor recombination) and 1.540–1.600 eV (free electron and bound/free excitonic recombination) grows by factors of 8 and 14, respectively. At the same time, the emission is dominated by donor-acceptor pair recombination in the zones without RIBE, whereas is dominated by eA°-D°A° (emission broad band at 1.547 eV in dotted line of Fig. 2 and acceptor bound exciton recombination in the zones with RIBE attack. It is worth noting that eA°-D°A° and also A°X-D°X-FE recombination lines cannot be resolved in the experimental spectra of RIBE zones. In this case, two contributions can be deconvoluted by using Gaussian fits at 1.593 and 1.597 eV, the first one mostly due to A°X and the second to D°X-FE.

A straightforward question now is the origin of such changes between the PL spectra in both zones of the CdTe surface.The RIBE attack could introduce nitrogen impurities acting as acceptors if they substitute Te atoms.[11] In this case, an increase of the overall PL intensity can be expected if an increase of the acceptor concentration in the same proportion takes place. On the other hand, we cannot resolve eA° and D°A° contributions, as also occurs in the case of D°X and FE transitions. It could imply a simultaneous increase of acceptor and donor impurities, but we cannot say in which degree the donors either were in the sample, but not participating in the recombination, or were introduced by the RIBE process. The TRPL results will support the hypothesis, as explained below.

Figure 3 shows PL transients representative of the free/bound exciton recombination (a) and donor-acceptor pair recombination (b). The PL decay time in the zones without RIBE attack is typically longer than that measured in the zones with RIBE attack. Something similar occurs for lower detection energies (1.447–1.555 eV), characterizing eA°, D°A°, and DAP recombination processes. Indeed, the PL transients over this broad energy range have an aspect similar to those shown in Fig. 3(b): a fast PL transient over the first 170 ps (rise plus decay), approximately, followed by a slow PL decay, longer for lower detection energies. On the one hand, we associate these slow decays to the impurity related recombination processes. On the other hand, the fast PL transients are close similar to the temporal response of the streak camera to the laser diffusion at the CdTe surface (system response), and it can be attributed to the fast transfer of carriers toward acceptor impurity levels prior to give rise to the different recombination paths observed in Fig. 2. The strong coupling with optical LO phonons in this material (Huang–Rhys factor around 1 or above[13,14]) would be responsible of that fast carrier transfer and also the appearance of replica of the main D°A° and DAP recombination chan-

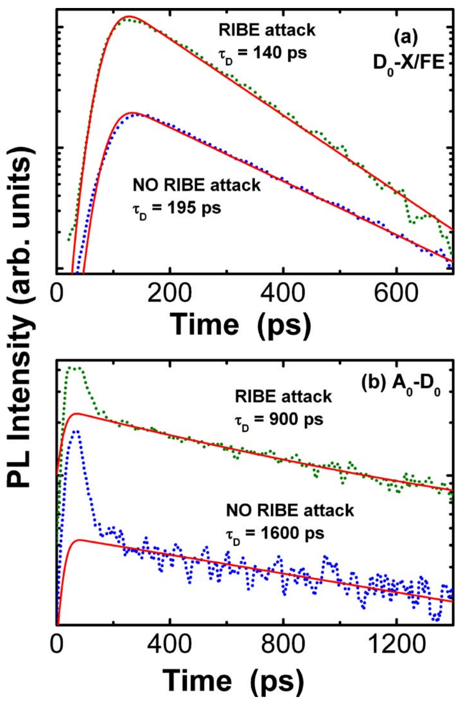

FIG. 3. (Color online) PL transients at 10 K under near resonant conditions and low excitation power in the zones with and without RIBE attack representative of the donor-bound-exciton/free-exciton (detection at about 1.596 eV) (a) and donor-acceptor pair (b) recombination. Continuous lines are the best exponential fits to the experimental PL transients.

nels. The D°A° and DAP recombinations are characterized with larger decay times when lower is the emission energy. Any discontinuity is observed at their corresponding phonon replica.

As a matter of fact, the PL decay times are shorter in the zones with RIBE than in the zones without RIBE attack over the whole emission energy. If the only reason for the increase of the PL intensity in these zones was the increase of the quantum efficiency and hence the increase of the nonradiative time, we should measure longer decay times in the zones with RIBE attack. This is because the relation between radiative, assumed for the moment to be the same at zones with and without RIBE attack, nonradiative and the effective decay time τ_D is

$$\frac{1}{\tau_D} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}. \tag{1}$$

However, this is not the case. We observe just the contrary, decay times larger in the zones without than in zones with RIBE attack. The simplest hypothesis to reconcile continuous wave and time resolved PL results is the increase of the impurity concentration due to the RIBE process in a factor around 10 in order to explain the observed intensity increase of the eA°, D°A°, and DAP bands. The greater increase of the eA° and D°A° bands is consistent with the above suggested assumption of an acceptor production from nitrogen atoms present in the etching plasma. In this way, it is possible a simultaneous increase of the PL intensity and a decrease of the nonradiative times after the RIBE attack of CdTe. This is just the results shown in Fig. 4, where the dashed line represent decay time values estimated by using

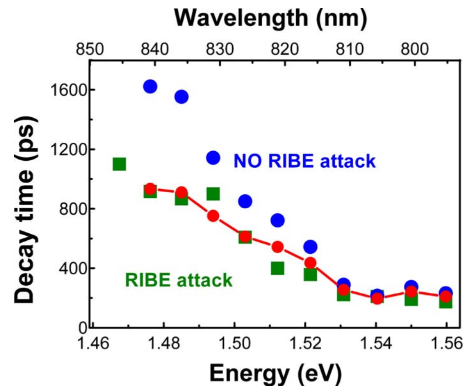

FIG. 4. (Color online) Emission energy dependence of the PL decay time in the zones without (circles) and with (squares) RIBE attack. The dotted line corresponds to an estimate of the decay time by using Eq. (1).

Eq. (1), considering as radiative time the decay times measured in the zones without RIBE attack and using a nonradiative time around 2200 ps. This is made by assuming that the radiative recombination times of the different processes in CdTe after RIBE attack do not depend significantly on the impurity concentration, at least for that observed factor of 10

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