Effect of thermal annealing for CuInSe₂ layers obtained by photoluminescence measurement

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Abstract: High quality CuInSe₂ (CIS) were grown on GaAs substrate by using the hot wall epitaxy method. The behavior of point defects in the CIS layer investigated by using photoluminescence (PL) at 10 K. Point defects originating from V_{Cu}, V_{Se}, Cu_{don}, and Se_{don} were classified as donor or acceptor types. These PL results also led us to confirm that the p-type CIS layer had obviously converted into n-type after the Cu atmosphere treatment. Finally, we found that the In in the CIS layer did not form the native defects, because In existed in the form of stable bonds in the CIS layer.

Key Words: post annealing, photoluminescence, point defect, hot wall epitaxy, copper Indium diselenide

1. Introduction

Ternary compounds including copper indium diselenide (CuInSe₂, CIS), which crystallizes to the chalcopyrite structure, have received considerable attention in recent years because of its applications in photovoltaic devices [1-3].

In this paper, we grew CIS(112)/GaAs(100) heteroepitaxial layers by using the hot wall epitaxy (HWE) method, which is able to achieve growth at low temperatures. To track the predominant point defects in the CIS layers, we conducted the photoluminescence (PL) measurements through post-annealing in various atmospheres. Based on these results, we discussed the behavior of the defects in the CIS layers.

2. Results and discussion

2.1. PL effect of the post-annealed CIS layers

To track the behavior of point defects on the as-grown CIS layer, we compared the PL spectra with the as-grown CIS and annealed CIS layers. Figure 1 presents the PL spectrum of the CIS:In layer. This means that In is not related to the formation of the native defect in the sample because In forms more covalent bonds than Cu and Se in chalcopyrite structure semiconductors, i.e., In participates more in the formation of pre-covalent and less-ionic chalcopyrite compounds than Cu and Se. Therefore, the above evidence indicates that the In atoms exist as a stable element in the CIS after the layer growth. Furthermore, it means that point defects related to In will be not observed in the CIS layers[4].

Figure 2 shows the PL spectrum of the CIS:Cu layer. We found that the peak corresponding to the (A°, X) completely disappeared in CIS. This disappearance indicates that (A°, X) is certainly associated with the acceptor level of V_{Cu} or V_{In}. The probable cause of these defects is V_{Cu} because In is the stabilizing element in the CIS layer. Also, the (D°, X) emission showed the dominant
3. Conclusions

The CIS(112) layers on GaAs(100) substrate were grown using the HWE method. From the PL measurement of the as-grown sample and the samples post-annealed in various atmospheres, the (D\textsuperscript{0}, X) emission reached its most dominant intensity in the PL spectrum of the CIS:Cu, while the (A\textsuperscript{0}, X) emission completely disappeared in the CIS:Cu. However, the (A\textsuperscript{0}, X) emission maintained its dominant intensity in the CIS:Se. Based on these results, the (D\textsuperscript{0}, X) and the (A\textsuperscript{0}, X) emissions were found to originate from the V\textsubscript{Se} or Cu\textsubscript{int} acting as a donor and the V\textsubscript{Cu} or Se\textsubscript{int} acting as an acceptor. Thus, we confirmed that the p-type CIS layer converted into n-type after the Cu atmosphere treatment. The emissions related to DAP originated from the interaction between donors such as V\textsubscript{Se}, Cu\textsubscript{int} or their complexes and acceptors such as V\textsubscript{Cu}, Se\textsubscript{int} or their complexes. The SA emission nearly disappeared after the Cu ambient annealing but that on the sample after the Se atmosphere annealing showed shapes similar to the as-grown CIS layer. This means that the origin of the SA emission is related to the V\textsubscript{Cu}, Se\textsubscript{int} or their complexes, which acted as acceptors. From the result of PL measurement on the CIS:In specimen, the In in CIS layer is not related to the formation of its native defects because In is a stable ingredient in the CIS.

References