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Growth of Arsenic-Doped Cadmium Telluride Epilayers by Metalorganic Chemical Vapor Deposition

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Abstract—We have studied arsenic incorporation from tris(dimethylamino)arsine into epitaxial CdTe layers in a metalorganic chemical vapor deposition (MOCVD) process. Arsenic incorporation into the layers has been shown to depend on the crystallographic orientation of their growth. Incorporation effectiveness increases in the order (111)B < (211)B < (100) < (310) < (211)A. Arsenic concentration in the CdTe layers is proportional to the tris(dimethylamino)arsine flow rate to the power 3/2. The dependence of arsenic incorporation on the ratio of the metalorganic tellurium and cadmium precursors in the vapor phase suggests that arsenic is incorporated predominantly into the anion sublattice. The maximum concentration of free charge carriers, $p_{295} = (1–2) \times 10^{17}$ cm^{-3}, was observed after annealing of the arsenic-doped CdTe layers in an argon atmosphere.

Keywords: cadmium telluride, doping, arsenic, tris(dimethylamino)arsine, epitaxial layer

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INTRODUCTION

Cadmium telluride (CdTe) is a promising semiconductor material which is successfully used in the fabrication of thin-film solar cells and gamma-ray and X-ray detectors [1, 2]. CdTe is among the few II–VI compounds that can have both *n*- and *p*-type conductivity. Crucial for advances in the fabrication of efficient CdTe-based solar cells is the ability to produce *p*-type layers with high carrier concentration. Among acceptor dopants, a great deal of attention is paid to the Group V elements (N, P, and As). Arsenic is the most suitable among these dopants because the energies needed to incorporate N and P atoms into the CdTe lattice are rather high.

In the vapor phase growth of CdTe layers, volatile arsenic compounds are commonly used as arsenic precursors: arsine and its derivatives [3, 4], including tris(dimethylamino)arsine (TDMAAs), $[(CH_3)_2N]_3As$ [5, 6]. The main advantages of TDMAAs are its relatively low decomposition temperature (50% decomposition at 380°C [7]) and the reduced probability of the formation of As–H and As–C complexes (which may neutralize the electrical activity of the arsenic dopant) in the deposit.

For arsenic to act as an acceptor in CdTe, it should occupy tellurium sites (As_{Te}). It will then be a shallow impurity with an ionization energy of 92 meV [8]. To facilitate the incorporation of arsenic into the anion sublattice of cadmium telluride, CdTe layers are typically grown in the presence of excess Cd, which increases the concentration of tellurium vacancies, V_{Te}. Theoretical calculations [9] suggest however that this increases the probability of the formation of cadmium interstitials, Cd_i, which act as doubly charged donors and compensate for the electrical activity of the arsenic. On the other hand, CdTe growth in the presence of excess tellurium increases the As_{Te} formation energy [9], thereby reducing the amount of arsenic incorporated into the deposit.

In spite of extensive studies, the behavior of arsenic impurities in CdTe has not yet been fully understood, and the degree of its electrical activity remains not very high.

The objectives of this work were to study general trends in the incorporation of arsenic atoms from TDMAAs into CdTe layers in a metalorganic chemical vapor deposition process in relation to deposition conditions (dopant precursor concentration, crystallographic orientation of the substrate, and relationship between metalorganic precursors) and assess the effect of subsequent thermal annealing on the concentration of free charge carriers in CdTe layers.

EXPERIMENTAL

Epitaxial CdTe layers were grown in a vertical quartz reactor from high-purity dimethylcadmium (DMC) and diethyltellurium (DET) vapors at a total pressure of 20 kPa and a substrate temperature of 350–360°C (metalorganic chemical vapor deposition (MOCVD) process) [10]. The carrier gas used was Pd-diffused hydrogen, with a total flow rate of 3 L/min (normal conditions). The layers were grown on semi-insulating GaAs substrates with the crystallographic orientations (100), (111)B, (310), (211)B, and (211)A. To preclude the influence of the diffusion of substrate components into the growing layer, undoped (buffer) CdTe layers at least 2 μm in thickness were first grown on the substrate, and then CdTe:As was deposited.

The arsenic-doped CdTe layers were produced at a constant DMC flow rate of 4×10^{-5} mol/min. The DET flow rate was varied from 2×10^{-5} to 8×10^{-5} mol/min (the DET/DMC molar ratio was thus varied from 0.5 to 2). The TDMAAs (99.999%) flow rate was varied in the range from 1×10^{-8} to 1×10^{-6} mol/min. All of the CdTe layers thus grown were identical in crystallographic orientation to their substrates.

The thickness of the epitaxial CdTe layers was evaluated from their transmission spectra, which were measured on a Nicolet 6700 Fourier transform IR spectrometer.

The arsenic concentration profile across the CdTe layers was obtained by secondary ion mass spectrometry (SIMS) depth profiling. SIMS spectra were measured on a TOF.SIMS-5 time-of-flight secondary ion mass spectrometer. We recorded As, AsTe, and AsTe2 ion signal intensities. The arsenic content of the layers was evaluated as the ratio of the sum intensity of these signals to the CdTe ion signal intensity. The arsenic concentration (cm^{-3}) was determined from comparison with arsenic-implanted CdTe reference samples.

The room-temperature electrical parameters of the epitaxial CdTe layers were determined using Hall effect measurements by the van der Pauw method ($B = 0.5$ T). Ohmic contacts to p-CdTe were made by chemical deposition of gold from an aqueous $HAuCl_4 \cdot 4H_2O$ solution. To improve the electrical activity of the arsenic dopant, we carried out brief (1 to 30 min) anneals in a high-purity argon atmosphere ($p = 1$ atm) at temperatures from 200 to 500°C.

RESULTS AND DISCUSSION

Figure 1a shows arsenic concentration profiles across epitaxial CdTe layers grown on GaAs(100) substrates at different TDMAAs flow rates at the reactor inlet. The arsenic concentration profile across the undoped sample can be used to evaluate the background level of the epitaxy unit and the detection limit of SIMS. Arsenic impurities in CdTe layers can be determined reliably using the TOF.SIMS-5 at concentrations above 1×10^{17} cm^{-3}.

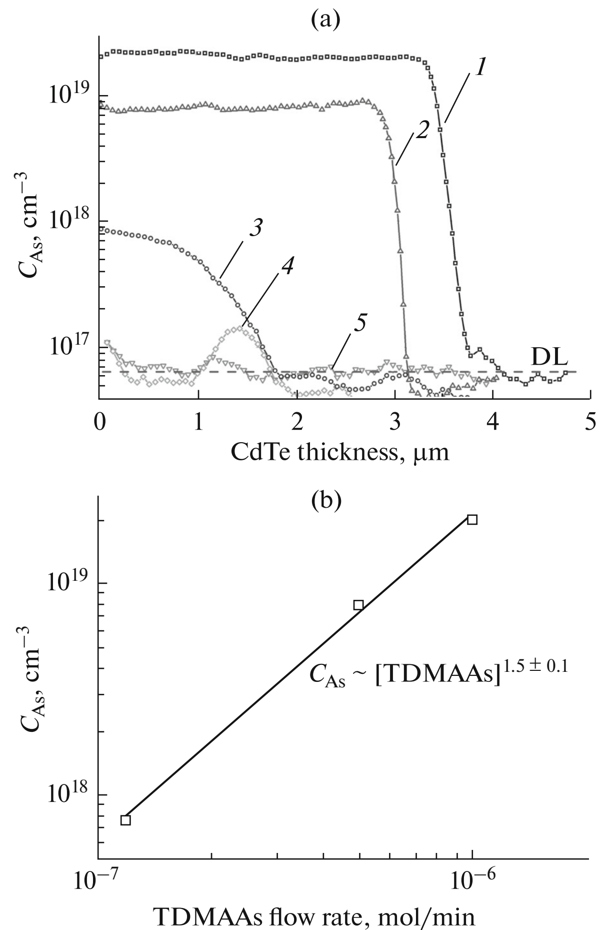

Fig. 1. (a) Arsenic concentration profiles across epitaxial CdTe layers grown on GaAs(100) at different TDMAAs flow rates (mol/min) at the reactor inlet (DET/DMC = 1): (*1*) 1×10^{-6}, (*2*) 5×10^{-7}, (*3*) 1.2×10^{-7}, (*4*) 1×10^{-8}, (*5*) 0; (b) arsenic concentration as a function of TDMAAs flow rate (DET/DMC = 1) for epitaxial CdTe layers on GaAs(100).

The arsenic concentration in the epitaxial CdTe layers grown at a TDMAAs flow rate of 1.0×10^{-8} mol/min does not exceed the detection limit of SIMS, $(6–7) \times 10^{16}$ cm^{-3}. Increasing the TDMAAs flow rate to 1.2×10^{-7} mol/min led to an increase in arsenic concentration in the layers to $\sim 10^{18}$ cm^{-3}, so the arsenic could be determined reliably. The CdTe layers grown at TDMAAs flow rates of 5×10^{-7} and 1×10^{-6} mol/min had uniform dopant concentration profiles with a sharp boundary between the doped and undoped regions. The arsenic concentration C_{As} in the CdTe layers is a power-law function of TDMAAs flow rate (Fig. 1b):

$$C_{As} \sim [TDMAAs]^{a}, \quad (1)$$

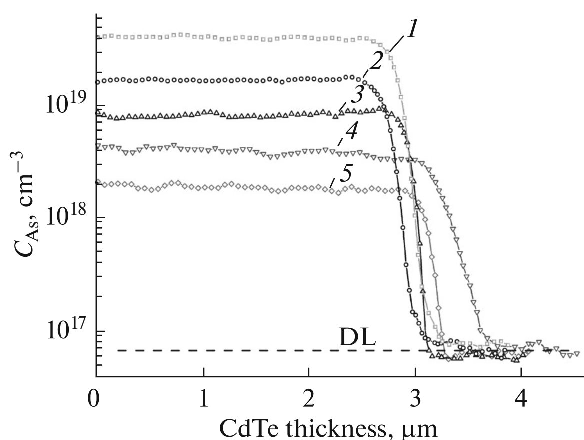

Fig. 2. Arsenic concentration profiles across epitaxial CdTe layers of various crystallographic orientations on GaAs (DET/DMC = 1, TDMAAs flow rate of 5×10^{-7} mol/min): (*1*) (211)A, (*2*) (310), (*3*) (100), (*4*) (211)B, (*5*) (111)B.

where $a = 1.5 \pm 0.1$. In a number of studies concerned with doping of GaAs in an MOCVD process, the dopant concentration in layers as a function of the dopant precursor concentration in the vapor phase was observed to deviate from linearity (with both $a < 1$ and $a > 1$) [11]. The deviation of a from unity was not interpreted, so it is difficult to identify the rate-limiting step of the complex, multistep process, involving a large number of chemical species. Rowlands et al. [5] investigated the incorporation of arsenic from TDMAAs into CdTe layers on glass during deposition from DMC and diisopropyltellurium vapors at 390°C, similar partial pressures of the metalorganic precursors, and a total pressure of 1 atm. They obtained a power-law dependence of the form (1) with $a = 2$ and assumed that, when CdTe was doped using TDMAAs, the rate-limiting step of the process was the formation of $[(CH_3)_2N]_2As \times As[N(CH_3)_2]_2$ dimers in the vapor phase. However, the As–As bond energy (382 kJ/mol) is lower than the As–N bond energy (489 kJ/mol) [12], so the dimer is less stable than the monomer.

The lower value of a in this study compared to that obtained by Rowlands et al. [5] seems to be due to distinctions in deposition conditions (reduced pressure and temperature) and the rate-limiting step of the doping process. According to Salim et al. [7], the rate-limiting steps of the thermal decomposition of TDMAAs are homolysis with $(CH_3)_2N^{\bullet}$ formation and the interaction of TDMAAs molecules with the forming free radicals ($H^{\bullet}$ and $(CH_3)_2N^{\bullet}$). In our case, this process is significantly complicated by the concurrent decomposition of TDMAAs, DMC, and DET and the catalytic effect of the deposition surface. This may cause the exponent a to deviate from unity.

Figure 2 shows arsenic concentration profiles across epitaxial CdTe layers of various crystallographic orientations. Arsenic incorporation strongly depends on the orientation of the growing layer and cannot be accounted for by the dependence of the CdTe deposition rate on the growth direction. This indicates that the rate of dopant incorporation is limited by the kinetics of surface processes rather than by dopant delivery to the substrate. The dependence of dopant incorporation on the crystallographic orientation of growth is typically accounted for in terms of different configurations of dangling surface bonds and differences in adsorption and desorption energies of dopant atoms on the crystal surface. Arsenic concentration in layers of different orientations increases in the order (111)B < (211)B < (100) < (310) < (211)A. The largest incorporation is observed on substrates with the polar orientation (211)A, whose surface is saturated with Cd atoms, as well as on substrates with the nonpolar orientations (310) and (100). At the same time, the incorporation of arsenic impurities is minimal for the tellurium-enriched substrate surfaces (211)B and (111)B. Arsenic concentration in the CdTe(211)A layers is about one order of magnitude higher than that in the CdTe(211)B layers.

These results are in contradiction with data reported by Svob et al. [13], who used AsH_3 to dope CdTe in an MOCVD process. They used (100), (511)A,B, (311)A,B, and (211)A,B GaAs substrates. The maximum arsenic incorporation was observed on the GaAs(100) substrates, and the minimum incorporation was observed at the (211)A orientation. Note that the arsenic concentration was higher on the B side than on the A side. These results were accounted for by the formation of a $(CH_3)_2Cd–AsH_3$ intermediate adduct in the vapor phase and arsenic incorporation into a layer in the vapor phase with a cadmium atom, Cd–As. The distinction of our data can be explained by a different mechanism of arsenic incorporation into CdTe layers in the course of doping from TDMAAs. Clearly, in the case of atomic arsenic incorporation into the tellurium sublattice, the A side of polar substrates and nonpolar substrates will have an advantage over the B side of substrates because the latter has a surface "saturated" with tellurium (the lowest concentration of tellurium vacancies).

Figure 3 shows an arsenic concentration profile across an epitaxial CdTe layer that was grown at a varied DET/DMC ratio in the vapor phase. The DET/DMC ratio was varied from an excess of DET (DET/DMC = 2) to equal partial pressures of the metalorganic compounds (DET/DMC = 1) and to an excess of DMC (DET/DMC = 0.7). According to data in the literature, varying the ratio of the metalorganic tellurium and cadmium precursors in the vapor phase allows one to effectively change the density of native defects in CdTe layers, changing dopant incorporation conditions. Raising the cadmium (DMC) partial pressure in CdTe growth leads to an increase in the concentration of tellurium vacancies V_{Te} and interstitial cadmium Cd_i.

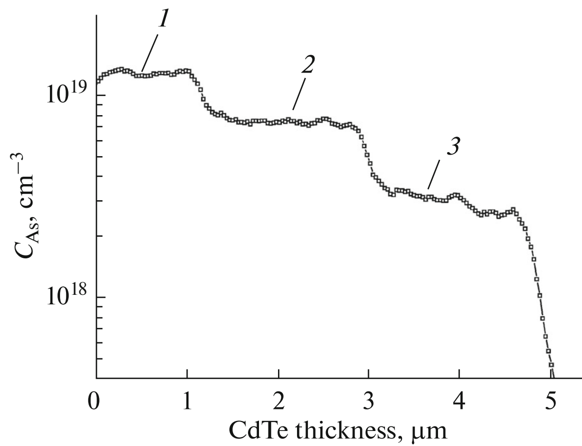

Fig. 3. Arsenic concentration profile across an epitaxial CdTe layer grown at a varied DET/DMC ratio: (*1*) 0.7, (*2*) 1, (*3*) 2 (TDMAAs flow rate of 5×10^{-7} mol/min).

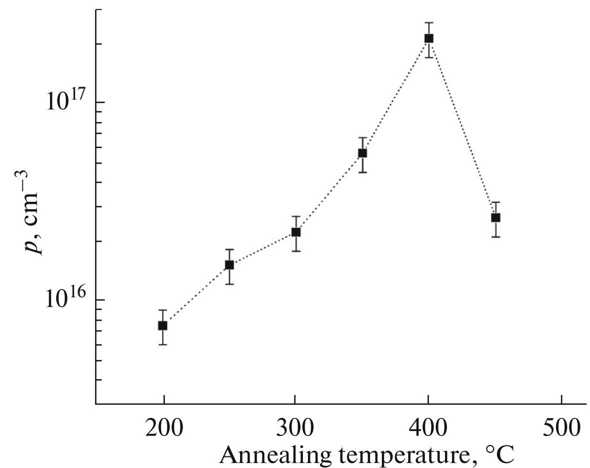

Fig. 4. 295-K hole concentration as a function of annealing temperature (argon atmosphere, annealing time of 15 min) for epitaxial CdTe(100):As layers.

The present data demonstrate that reducing the DET/DMC ratio in the process of growth from 2 to 0.7 (at a TDMAAs flow rate of 5×10^{-7} mol/min) increases the arsenic concentration in the layers from 3×10^{18} to 1.3×10^{19} cm^{-3}.

The observed effects of orientation and DET/DMC ratio on arsenic incorporation suggest that arsenic is incorporated predominantly into the anion sublattice: As_{Te}.

Under the conditions of this study, the undoped CdTe layers have semi-insulating properties: their resistivity exceeds 10^5 Ω cm. The as-grown epitaxial arsenic-doped CdTe layers were *p*-type, with a carrier concentration of $\leq n \times 10^{15}$ cm^{-3}, which was essentially independent of the arsenic concentration in the layers (in the range 10^{17} to 10^{19} cm^{-3}). Thus, the fraction of electrically active arsenic in these layers did not exceed 0.1–1%. Such behavior may be due to arsenic compensation by electrically active native defects, such as Cd_i, and the formation of neutral complexes with arsenic through the breaking of two neighboring cation–anion bonds and the formation of an additional As–Te bond, possessing donor properties (AX centers [14]).

To increase the fraction of electrically active arsenic by changing the status of native defects in CdTe and breaking down possible complexes of arsenic with native defects, we carried out series of anneals. We annealed epitaxial CdTe(100) layers grown at DET/DMC = 1 and having an initial arsenic concentration of 2×10^{18} cm^{-3}.

The results of annealing the epitaxial CdTe layers for 15 min in a high-purity argon atmosphere at temperatures from 200 to 500°C are presented in Fig. 4. The maximum carrier concentration, (1–2) × 10^{17} cm^{-3}, was observed at an annealing temperature of 400°C. With increasing annealing temperature, the concentration of free charge carriers decreases, presumably because of the formation of lattice defects with deep levels. After annealing at 500°C, the samples had high resistivity.

Figure 5 illustrates the effect of annealing time on the electrical properties of the epitaxial CdTe layers during annealing in an argon atmosphere at a temperature of 400°C. The largest increase in carrier concentration occurs during the first 15 min of annealing, and then the carrier concentration gradually decreases.

We examined the effect of gaseous atmosphere composition (Ar or H_2) on the results of annealing epitaxial CdTe layers for 15 min at 450°C. Annealing increased the concentration of free charge carriers from 2×10^{15} cm^{-3} to 1.8×10^{16} cm^{-3} in argon and to

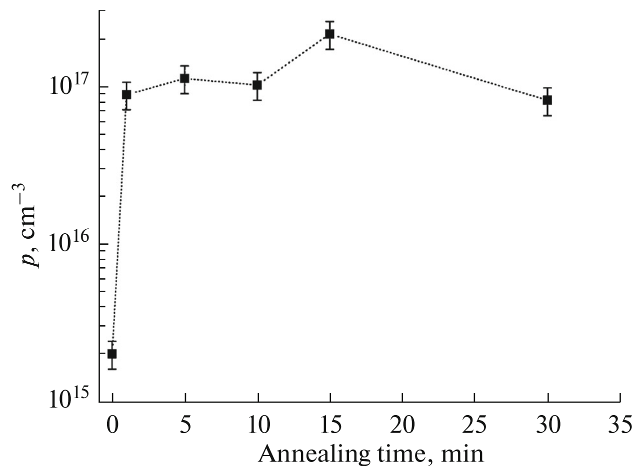

Fig. 5. 295-K hole concentration as a function of annealing time (argon atmosphere, annealing temperature of 400°C) for epitaxial CdTe(100):As layers.

2.1×10^{16} cm^{-3} in hydrogen. To within the uncertainty in our measurements (15–20%), the composition of the annealing atmosphere has no effect on the electrical properties of the epitaxial CdTe layers.

We believe that the electrical activity of arsenic in the epitaxial CdTe layers is limited primarily by the compensation of charge carriers by native defects (the most likely candidates are Cd_i and Cd_i–As complexes) and the formation of AX centers.

CONCLUSIONS

We have studied arsenic incorporation from TDMAAs into epitaxial CdTe layers in an MOCVD process. Arsenic concentration in the epitaxial CdTe layers has been shown to be proportional to $[TDMAAs]^{1.5}$ in the vapor phase at TDMAAs flow rates in the range from 1×10^{-7} to 1×10^{-6} mol/min. We have obtained epitaxial CdTe layers with arsenic concentrations above 10^{19} cm^{-3}.

Arsenic incorporation into the epitaxial CdTe layers has been shown to be orientation-dependent, which suggests that the rate of the process is limited by kinetic stages on the surface. Arsenic concentration in the epitaxial CdTe layers of different crystallographic orientations increases in the order (111)B < (211)B < (100) < (310) < (211)A. The difference in arsenic concentration between the CdTe(111)B and CdTe(211)A layers exceeds one order of magnitude.

Reducing the DET/DMC ratio in the vapor phase from 2 to 0.7 increases the arsenic concentration in the epitaxial CdTe layers by four times, which confirms that arsenic is incorporated primarily through tellurium vacancies.

The maximum concentration of free charge carriers, $p_{295} = (1–2) \times 10^{17}$ cm^{-3}, in the epitaxial CdTe layers was observed after annealing of the doped layers for 1–15 min at a temperature of 400°C. The concentration of free charge carriers after annealing was about 10% of the total arsenic concentration in the layers.

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