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## Passivation of CdHgTe surface using low-temperature plasma-enhanced atomic layer deposition of HfO<sub>2</sub>

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Received April 2, 2024

Revised April 25, 2024

Accepted April 26, 2024

Thin films of hafnium oxide formed by plasma-enhanced atomic layer deposition on the surface of mercury-cadmium telluride in the temperature range of 80–160°C were studied. To characterize the properties of the films and the insulator–semiconductor interface, the following techniques were used: X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), atomic force microscopy (AFM), spectral ellipsometry, and analysis of capacitance–voltage characteristics (C–V) of metal–insulator–semiconductor structures. The paper presents the dependences of the studied parameters on the insulator deposition temperature.

**Keywords:** CdHgTe, HfO<sub>2</sub>, plasma-enhanced atomic layer deposition, surface passivation, metal–insulator–semiconductor.

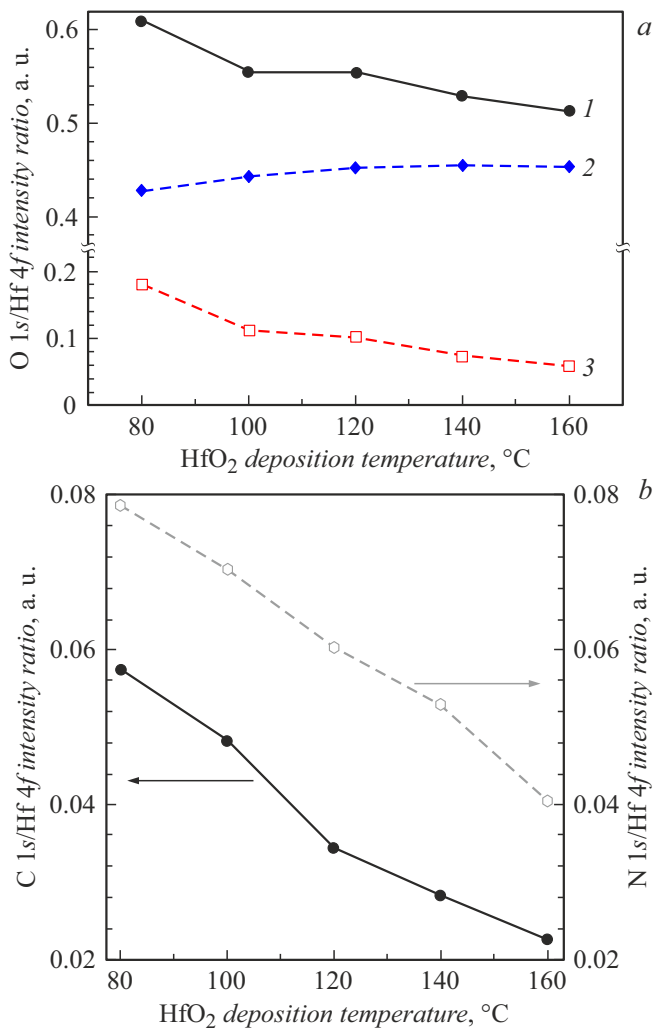
DOI: 10.61011/TPL.2024.08.58917.19937

Mercury cadmium telluride (CdHgTe) is one of the key semiconductor materials used for the production of infrared devices [1–3] and the development of terahertz photonics devices [4,5]. Surface passivation remains one of the most important lines of development of manufacturing technology for CdHgTe-based photodetector devices. The materials used most often as passivating coatings for CdHgTe are CdTe [5,6] and ZnS [7,8]. Of these two, CdTe forms a higher-quality interface with CdHgTe, which is evidenced by low values of the surface state density, the built-in charge density, and the rate of surface recombination. However, it has significant disadvantages in a small valence band offset (and, consequently, low height of the potential barrier for electrons), which is below 0.5 eV; low resistivity (compared to dielectric films); and infeasibility of selective etching of the passivation coating when windows are formed in it for ion implantation and metallization. Thus, the search for new methods of passivation of CdHgTe and the development of existing techniques are ongoing.

Atomic layer deposition (ALD) or, more specifically, plasma-enhanced atomic layer deposition (PE-ALD) is one of the most technologically advanced methods of low-temperature application of dielectric coatings. This technology is used widely for passivation of the surface of semiconductors with films of Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, TiO<sub>2</sub>, etc. [9]. Atomic layer deposition of just Al<sub>2</sub>O<sub>3</sub> [10] and ZnS [7] on CdHgTe has been reported in literature, although hafnium oxide appears to be a promising alternative. The aim of the present study is to examine the properties of both thin HfO<sub>2</sub> films formed by PE-ALD on CdHgTe at temperatures of 80–160°C and the resulting dielectric–semiconductor interface.

An undoped Cd<sub>0.22</sub>Hg<sub>0.78</sub>Te film was grown by molecular beam epitaxy on a Si(013) substrate and annealed for the purpose of vacancy doping ( $p \sim 1 \cdot 10^{16} \text{ cm}^{-3}$ ). The wafer was divided into many identical samples, and thin films (5–20 nm) of HfO<sub>2</sub> were deposited onto them by PE-ALD using the tetrakis(ethylmethylamino)hafnium (TEMAH) precursor at different substrate temperatures (80, 100, 120, 140, and 160°C) [11]. The thickness and the refraction index of the deposited films were monitored *ex situ* with a Woollam EC-400 spectral ellipsometer. The chemical composition was analyzed by X-ray photoelectron spectroscopy at a ProvenX-ARPES setup fitted with a monochromatized AlK<sub>α</sub> radiation source (1486.71 eV). Surface contaminants were removed from films prior to analysis by irradiating them with an Ar<sup>+</sup> (800 eV) ion beam. The electron beam source (1000 eV) was used for electron energy loss spectroscopy (EELS). The surface morphology was studied with a Bruker MultiMode 8 atomic force microscope (AFM). Metal–insulator–semiconductor (MIS) structures with indium gates were fabricated using photolithography, and their capacitance–voltage (C–V) characteristics were measured with an Agilent B1500A analyzer at a sample temperature of 77 K.

Photoelectron line Hf 4*f* (17–19 eV) in the spectra of all the studied films with a thickness of ~ 20 nm is represented by a single doublet (spin-orbit splitting, 1.67 eV; full width at half maximum, 1.2 eV; area ratio, 4:3) corresponding to oxidized state Hf<sup>4+</sup>. It is known from our earlier work [11] and other sources [12] that the O 1*s* (531 eV) line of ALD HfO<sub>2</sub> films contains two components: the most intense one at a lower binding energy corresponds to hafnium oxide, while the less intense one at a higher binding energy corresponds to –OH groups, absorbed water, and other by-



**Figure 1.** Ratios of areas of components of line O 1s (1 — total area of O 1s; 2 — component corresponding to hafnium oxide; 3 — component corresponding to oxidation by-products) (a) and lines C 1s and N 1s (b) to the Hf 4f line area.

products of precursor oxidation. It follows from Fig. 1, a, which shows the calculated ratios of areas of the O 1s line components to the Hf 4f area at different deposition temperatures, that an increase in substrate temperature leads to a reduction in the fraction of oxygen corresponding to oxidation by-products; however, the  $[O^{2-}]/[Hf]$  ratio, which increases in this case, reaches saturation already at 120°C. In addition to oxygen and hafnium, the film contains impurity carbon and nitrogen. The concentration of C and N decreases significantly with an increase in deposition temperature (Fig. 1, b). Accurate calculation of relative concentrations of film components requires calibration of the relative atomic sensitivity coefficients for the used experimental setup. It is known that low-temperature HfO<sub>2</sub> films are often characterized by an oxygen deficiency, and the concentration of impurities in them may reach tens of percent [13], exerting a negative influence on the dielectric properties of films.

The approximate band gap width of the deposited dielectric [14] was estimated by EELS at 5.8 eV for all samples. This value agrees with literature data, although the spectra have a feature in the energy loss range of 2–3 eV that may be attributed to the presence of defect levels in the band gap of the obtained films. Valence band offset  $\Delta E_V$  at the HfO<sub>2</sub>–CdHgTe interface was determined from photoelectron spectra based on the shift of the valence band edge and remained approximately equal to 2.8 eV regardless of the deposition temperature. With the band gap width of Cd<sub>0.22</sub>Hg<sub>0.78</sub>Te at room temperature (0.181 eV) taken into account, the estimate of conduction band offset  $\Delta E_C$  is also close to 2.8 eV.

According to AFM data, the surface of deposited films does not have any pronounced morphological features and matches the original CdHgTe film surface. With an increase in deposition temperature from 80 to 160°C, roughness  $R_a$  decreased from 0.98 to 0.85 nm (the original surface roughness was 0.84 nm).

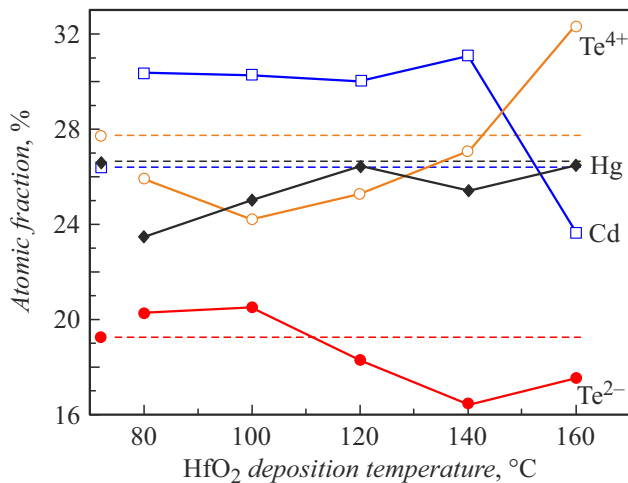
To study the changes in chemical composition of CdHgTe near the interface with HfO<sub>2</sub>, structures with a thinner coating ( $\sim 5$  nm) were fabricated, and relative atomic sensitivity coefficients  $S$  of the Te 3d, Cd 3d, and Hg 4f lines were pre-calibrated (1, 0.78, and 0.876, respectively). Known expressions for the dependence of the intensity of photoelectron lines on the thickness of a film on the substrate surface [15] were used to derive the following expression needed to take into account the different degrees of attenuation of their photoelectron signal in propagation of electrons with different mean inelastic scattering lengths  $\lambda$  through a film on the surface:

$$I_{i,c} = I_{i,m}(1 - I_{Hf,m}/I_{Hf,max})^{-\lambda_{Hf}/\lambda_i},$$

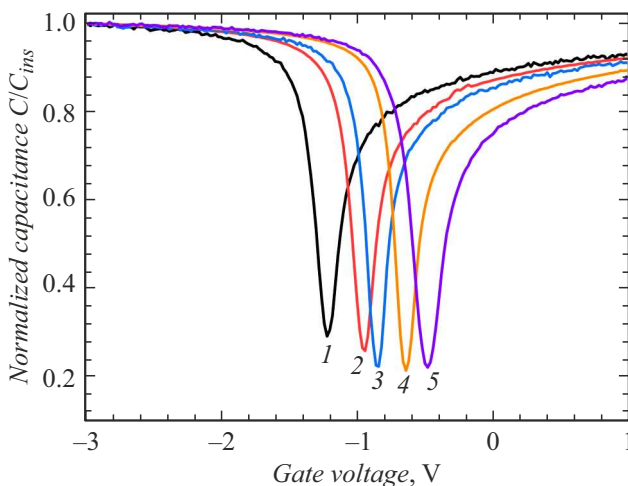
where  $I_{i,m}$  and  $I_{i,c}$  are the measured and corrected intensities of photoelectron line  $i$ ;  $I_{Hf,m}$  and  $I_{Hf,max}$  are the measured intensities of the hafnium line for thin ( $\sim 5$  nm) and thick ( $\sim 20$  nm) HfO<sub>2</sub> films, respectively; and  $\lambda_{Hf}$  and  $\lambda_i$  are the mean inelastic scattering lengths of electrons of hafnium and element  $i$  of the substrate in the HfO<sub>2</sub> film, respectively. With this correction introduced, the standard expression was used to calculate the relative concentrations of elements in matter:  $C_i = (I_{i,c}/S_i) / \sum I_{n,c}/S_n$ .

The calculated dependence of the chemical composition of CdHgTe near the interface with HfO<sub>2</sub> on the dielectric deposition temperature is shown in Fig. 2. At low temperatures ( $< 120^\circ\text{C}$ ), partial reduction of CdHgTe native oxide is observed; at higher temperatures, its thickness increases. In complete accord with the behavior of CdHgTe in vacuum observed earlier in [16], heating above 140°C resulted in decomposition of the material. However, the deposited film apparently inhibits the diffusion of mercury into vacuum, and no mercury deficiency is observed at high deposition temperatures.

The C–Vs of the obtained MIS structures have a typical low-frequency form at measurement signal frequencies up to 500 kHz (Fig. 3) and do not assume a high-frequency



**Figure 2.** Relative concentrations of  $\text{Te}^{4+}$  (in the composition of  $\text{CdHgTe}$  native oxide),  $\text{Te}^{2-}$  (in the composition of  $\text{CdHgTe}$ ), Cd, and Hg atoms near the  $\text{HfO}_2$ – $\text{CdHgTe}$  interface as functions of the dielectric deposition temperature. Dashed lines denote the corresponding concentrations in the near-surface region of  $\text{CdHgTe}$  before the deposition of  $\text{HfO}_2$ .



**Figure 3.** C–Vs of In– $\text{HfO}_2$ – $p$ - $\text{CdHgTe}$  structures. The  $\text{HfO}_2$  deposition temperature is 80 (1), 100 (2), 120 (3), 140 (4), and 160 °C (5).

form at 5 MHz. The permittivity of  $\text{HfO}_2$  films was calculated based on the maximum capacitance: it increases monotonically from 8 to 11 with an increase in deposition temperature from 80 to 160 °C. The density of the negative built-in charge of the dielectric was calculated based on the flat-band voltage, which was determined by graphical differentiation of C–VCs [17], with account for the metal-semiconductor work function difference ( $\varphi_{ms} = -1.3$  eV). It turned out that this density increases from  $0.4 \cdot 10^{12}$  to  $2 \cdot 10^{12}$   $\text{cm}^{-2}$  with an increase in deposition temperature in the studied range. The calculation of the spectrum of surface states by capacitive methods is made difficult by the need to calculate an ideal C–V (with account for

such semiconductor features as non-parabolicity of bands, carrier degeneracy, and quantization of energy levels near the surface) and obtain a C–V of a high-frequency type. Since the lifetime of minority carriers in narrow-bandgap  $\text{Cd}_{0.22}\text{Hg}_{0.78}\text{Te}$  at liquid nitrogen temperature is on the order of just 10–100 ns, a measurement signal frequency exceeding the limit of the measuring equipment or deeper cooling of the structure under study are needed to establish the conditions for a high-frequency C–V.

We note in conclusion that an increase in deposition temperature leads, quite predictably, to an improvement of quality of  $\text{HfO}_2$  films in terms of their chemical composition and dielectric properties, although heating above 140 °C is critical for the  $\text{CdHgTe}$  structure. However, plasma-enhanced deposition of  $\text{HfO}_2$  at a temperature around 120 °C with the use of TEMAH and remote oxygen plasma appears to be a promising method for passivation and protection of  $\text{CdHgTe}$  surfaces. A  $\text{HfO}_2$  film forms high potential barriers ( $\sim 2.8$  eV) for both types of carriers at the interface with  $\text{CdHgTe}$  and, unlike the widely used CdTe, has high resistivity and breakdown voltage values. One important task remaining is to reduce the density of the built-in charge, which may be achieved by optimizing the initial dielectric deposition stages and/or performing preliminary treatment of the semiconductor surface.

## Funding

This study was supported by a grant from the Russian Science Foundation, project № 21-72-10134 (<https://rscf.ru/project/21-72-10134/>).

## Conflict of interest

The authors declare that they have no conflict of interest.

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*Translated by D.Safin*