Твердотельная электроника

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Al/nanocrystalline CeO_x/Si/Al structures for heterojunction photodetectors

A stable metal/nc-CeO_x/Si structures were fabricated and investigated for the creation of heterojunction photodetectors. The photosensitivity of obtained structures in the visible range was 330 μA/lm·V. The value of the interface state density was of $7 \cdot 10^{10}$ $cm^{-2} \cdot eV^{-1}$. DC dielectric constant of nanocrystalline CeO_x film was about 15. Thin (80 nm) cerium oxide films in Al/nc-CeO_x/Si/Al structures were obtained by the vacuum flash evaporation method. The effect of technological factors on the CeO_x films microstructure as well as on photoelectric properties of the Al/nc-CeO_x/Si/Al structures has been investigated. Electrophysical *and photoelectric properties of the Al/nc-CeO_x/Si/Al structures has been investigated. It was revealed that the nanocrystalline CeO_x layer in the obtained Al/nc-CeO_x/Si/Al structures is a semiconductor with an electronic conductivity. It's volume resistivity is within the range of 0.5-30 MOhm·cm.* Reference 9, figures 2.

Keywords: *heterojunction, nanocrystalline cerium oxide films, metal/oxide/semiconductor photodiode, Al/CeOx/Si/Al structure, CeOx.*

Introduction

Cerium oxide has become a promising material for silicon microelectronics because at least of three reasons: i) with its high dielectric constant (20–26), CeO_2 is considered as a candidate for replacing SiO_2 in silicon devices, for example, as a storage capacitor in dynamic random access memory devices; ii) excellent lattice match with silicon, which means a very good epitaxy on silicon; iii) good chemical stability, iiii) inexpensiveness [2,3,4]. However, to bring the CeO_2/Si system to the level of maturity needed for commercial devices, extensive investigations are still needed, especially on the structural characteristics of CeO_2 films after some standard microelectronics processes.

There are several candidates for possible materials to replace SiO_2: Si_3N_4, ZrO_2, YSZ, Ta_2O_5, HfOz, TiO_2, $SrTiO_3$. Each dielectric has its own advantages and disadvantages [6]. The cerium oxides have properties that match or exceed those of all the other materials listed and yet have been studied far less than all the others in terms of their use as a gate dielectric. Again it is clear that CeO_2 has properties equal or superior to those of the other materials shown above in terms of qualities for forming a silicon heterostructure [6].

But very little is known about cerium oxide and a great deal of research are needed to determine its utility as a silicon heterojunction material. In general the behavior of cerium oxides in thin film form prior to this effort was poorly understood. Based on the analysis of publications devoted to the study of cerium oxide films it also was determined that properties of the cerium oxide films and their quantitative relationships with the technological parameters are studied insufficiently.

The aim of this work was to prepare Al/nc-CeO_x/Si/Al structures and investigate the effect of technological factors on CeO_x films as well as on photoelectric and electrophysical properties of the received structures.

Experimental and Discussion

Thin (80 nm) cerium oxide films in Al/nc-CeO_x/Si/Al structures were obtained by the vacuum flash evaporation method from CeO_2 powder [8]. The substrates used were n- and p-type Si (111) wafers chemically cleaned by standard microelectronic technology process. Evaporation of CeO_x was carried out in vacuum ranging from 10^{-3} to 10^{-2} Pa. The temperature range was 175–300°C. [1,5,7].

Microstructure of the obtained CeO_x films was studied by transmission electron microscope (TEM) ПЕМ У-М (0.21 nm resolution, 125 kV accelerating voltage) and X-diffractometer DMAX - B Japan [5]. The structural properties of cerium oxide films have been studied using X-ray photoelectron spectroscopy (XPS) (SERIES 800 XPS, Kratos Analytical, X-ray tube with a magnesium anode (U9=12 kV, I=30 mA).

Photoelectric properties of the obtained structures based on the cerium oxide films were studied with the help of lux-ampere characteristics. Electrophysical properties of Al/nc-CeOx/Si/Al structures were studied by method of I-V (current-voltage) characteristics. The method of high-frequency C-V (capacitance-voltage) characteristics was used to study the CeOx/Si interface [5]. The measurements were carried out at the frequency of 12 MHz.

The XPS spectra (Fig. 1) of cerium oxide films deposited at 175^{0}C showed the characteristic peaks attributed to trivalent Ce^{3+} (forming Ce_2O_3) and weak peaks which correspond to tetravalent Ce^{4+} (forms CeO_2). These results correlate with the data obtained via TEM and X-ray diffraction (XRD) analyses which revealed that CeO_2 nanocrystals in an amorphous Ce_2O_3 matrix are formed at low substrate temperatures (T_s=175^{0}C). The amorphous phase is represented by Ce_2O_3, while nanocrystalline – by CeO_2 with face-centered cubic crystal lattice.

Comparison of the results obtained from TEM, XPS and XRD analyses for CeO_x films obtained at higher substrate temperatures T_s (200^{0}C and 300^{0}C) gives grounds to conclude that the “flash” method gave nanocrystalline films of CeO_2 (111) with the CaF_2 structural type with no amorphous phase inside them. Also TEM investigations of CeO_x films deposited at 300^{0}C revealed changes in film morphology. These changes are probably due to the defects caused by the mechanical stresses in CeO_x films.

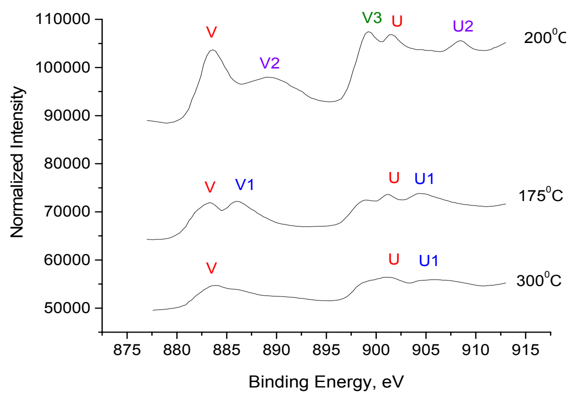

Fig. 1. Ce3d XPS spectra for cerium oxide films deposited at different substrate temperatures

Photovoltaic properties of any films, as well as of any structure on their basis, depend strongly on their microstructure, morphology and chemical composition, which are primarily determined by technological conditions of film fabrication. That's why we had studied the effect of substrate temperature and type on photovoltaic properties of the obtained Al/nc-CeO_x/Si/Al structures.

For investigation of photoelectric properties of the Al-ncCeO_x-Si-Al structures, lux-ampere characteristics were measured (Fig. 2). Al-ncCeOx-Si-Al structures were observed to have photoconductive properties when illuminated by a white light source. The calculated photosensitivity coefficients of the investigated structures on the basis of n-Si were higher compared to those of the structures on the basis of p-Si. Moreover the photosensitivity of Al/nc-CeO_x/Si/Al structures with p-Si did not depend on the substrate temperature, whereas n-Si structures with CeO_x film received at 200^{0}C showed a sufficient maximum of photosensitivity coefficient (330 μmA/lmV).

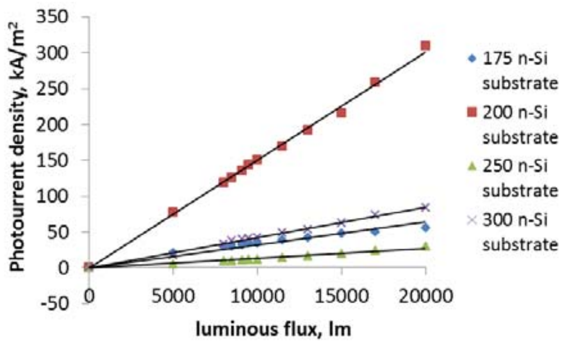

Fig. 2. Lux-ampere characteristics of Al/nc-CeO_x/Si/Al structures for different substrate temperatures of CeO_x film deposition

The method of high-frequency C-V characteristics was used to study the cerium oxide film/monocrystalline silicon interface. The investigation of the influence of substrate temperature on the interface state density (N_{ss}) revealed that N_{ss} increased with temperature rising from $7\cdot10^{10}$ to $1.9\cdot10^{11}$ $sm^{-2}\cdot eV^{-1}$. These results have a good correlation with our preliminary investigations of microstructural properties of CeO_x films and photoelectrical characteristics of the obtained MOS structures. It also was found that nc-CeO_x/Si structures where CeO_x film was obtained at 200^{0}C had the minimal value of N_{ss} ($7\cdot10^{10}$ $sm^{-2}\cdot eV^{-1}$), which is 15 times lower than the state density of

SiO_2/Si interface. Also typical value of the DC dielectric constant ε of the obtained CeO_x films was on the order of 10-15 which is 3-4 times higher than ε of the most commonly used SiO_2.

Thus from the results obtained from TEM, XPS, XRD-analyses, lux-ampere and C-V characteristics it can be concluded that increasing the substrate temperature from 175 to 200^{0}C leads to the growth in photosensitivity and reduction of interface states density at the film/substrate interface. This is caused by the transition from amorphous to nanocrystalline phase in CeO_x films and also by changes in the composition (from two-phase Ce_2O_3 and CeO_2 to single-phase CeO_2) of the cerium oxide films produced by the flash evaporation.

At the temperature of 200^{0}C the ordered nanocrystalline CeO_2 and Al/nc-CeO_x /Si/Al structures with the minimum value of the interface state density ($7\cdot10^{10}$ cm$^{-2}\cdot$eV^{-1}) and increased photosensitivity (330 μmA/lmV) are formed.

Further increase of the substrate temperature up to 250-300^{0}C leads to deterioration of the above mentioned properties due to the changes in the morphology and phase composition of the CeO_x films.

Based on the synthesized Al/nc-CeO_x/Si/Al structures we can develop new types of heterostructure diodes and photodiodes with improved electrical characteristics.

The specifics and difficulty of measuring of C-V characteristics led to the more thorough analysis of the structures. That entailed measuring of the DC I-V characteristics. The full analysis of I-V characteristics and their comparison with C-V will be presented in the next publications. We noted that the nc-CeO_x/Si junction has rectifying properties, and the resistance of high-resistivity layer of nanocrystalline CeO_x is within the 500-3000 Ohm, which corresponds to a volume resistivity of 0,5…30 MOhm·cm. It was also revealed that nanocrystalline CeO_x layer in the Al/nc-CeO_x/Si/Al structures is a semiconductor with electronic conductivity.

Conclusions

The present work shows that application of inexpensive flash evaporation method of CeO_x films deposition at relatively low temperatures (200 – 300 ^{0}C vs 1100 – 1300 ^{0}C needed for SiO_2 growth) not only simplifies the technology of producing of CeO_x films, but also enables fabrication of semiconductor/dielectric interfaces of enhanced quality. The latter plays an important role in MOS electronics and is very promising.

Al/CeO_x/Si/Al diode structures with improved electrical characteristics, namely - the value of interface state density of $7\cdot10^{10}$ sm$^{-2}\cdot$eV^{-1} (15 times lower than state density of SiO_2/Si interface) and a high value of DC dielectric constant ε=10÷15 (3÷4 times higher than that of the most commonly used SiO_2) - have been obtained.

It was experimentally determined, that the best characteristics for creation of heterojunction photodiode structures were demonstrated by the cerium oxide films deposited by explosive evaporation on n-type substrates at the temperature of 200^{0}C. These technological conditions promote formation of ordered nanocrystalline CeO_2 films and a minimum value of the interface state density ($7\cdot10^{10}$ cm$^{-2}\cdot$eV^{-1}) at the film/substrate interface which explains the increased photosensitivity.

Based on the synthesized Al/nc-CeO_x/Si/Al structures we have received new types of heterojunction photodiodes with increased photosensitivity (330 μmA/lmV).

Heterojunction photodiodes based on cerium oxide films obtained in this work could become a new basis for efficient photodetectors within the visible range, - in particular the photodetectors of luminescent signal, - instead of the costly and technologically complicated avalanche photodiodes and photomultiplier tubes.

The nc-CeO_x layer in the obtained Al/nc-CeO_x/Si/Al structures is a semiconductor with an electronic conductivity. It's volume resistivity is within the range of 0.5-30 MOhm·cm.

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Структури Al/нанокристалічний CeO_x/Si/Al для фотодетекторів на основі гетеропереходу

Виготовлено та досліджено структури метал/нанокристалічний-CeO_x/Si з метою створення фтотодетекторів на основі гетеропереходу. Фоточутливість отриманих структур у видимому діапазоні становить 330 мкА/Лм·В, густина поверхневих станів – на рівні $7 \cdot 10^{10}$ см$^{-2}$·еВ$^{-1}$. Діелектрична проникненість плівок CeO_x на постійному струмі становить 15. Тонкі (80 нм) плівки оксиду церію в структурах Al/nc-CeO_x/Si/Al були отримані методом «вибухового випаровування». Було досліджено вплив технологічних факторів на мікроструктуру плівок CeO_x, а також на фотоелектричні властивості структур Al/nc-CeO_x/Si/Al. Досліджено електрофізичні та фотоелектричні властивості структур Al/nc-CeO_x/Si/Al. Виявлено, що нанокристалічна плівка CeO_x в отриманих структурах Al/nc-CeO_x/Si/Al – це напівпровідник з електронним типом електропровідності та об'ємним опором в межах 0,5-30 МОм·см. Бібл. 9, рис. 2 .

Ключові слова: *гетероперехід, нанокристалічні плівки оксиду церію, МДН-фотодіод, структура Al/CeOx/Si/Al, CeOx.*

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Структуры Al/нанокристаллический CeO_x/Si/Al для фотодетекторов на основе гетероперехода

Изготовлены и исследованы структуры метал/нанокристаллический-CeOx/Si с целью создания фотодетекторов на основе гетероперехода. Фоточувствительность полученных структур в видимом диапазоне составляет 330 мкА/Лм·В, плотность поверхностных состояний – на уровне 7·1010 см-2·еВ-1. Диэлектрическая проницаемость пленок CeOx на постоянном токе достигает значения 15. Тонкие (80 нм) пленки оксида церия в структурах Al/nc-CeOx/Si/Al *были получены методом «взрывного испарения». Исследовано влияние технологических факторов на микроструктуру пленок CeOx, а также на фотоэлектрические свойства структур Al/nc-CeOx/Si/Al. Исследованы электрофизические и фотоэлектрические свойства структур Al/nc-CeOx/Si/Al. Обнаружено, что нанокристаллическая пленка CeOx в полученных структурах Al/nc-CeOx/Si/Al – это полупроводник с электронным типом электропроводности и объемным сопротивлением в пределах 0,5-30 МОм·см.* Библ. 9, рис. 2.

Ключевые слова: *гетеропереход, нанокристаллические пленки оксида церия, МДП-фотодиод, структура Al/CeOx/Si/Al, CeOx.*

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