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Pulsed laser deposition of HfO_2 and Pr_xO_y high-k films on Si(100)

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Abstract

Pulsed laser deposition was used to grow thin films of the high-k materials praseodymium oxide (Pr_xO_y) and hafnium oxide (HfO_2) on Si(100) due to its experimental simplicity and flexibility. Most important factors for technical application, such as film morphology and interface quality, were investigated by optical microscopy, atomic force microscopy and Raman spectroscopy.

During the growth process typical splashes, originating from the laser–target interaction, are embedded into the growing layer. The size of these splashes appears to depend strongly on the laser wavelength (355, 532, 1064 nm). The microscopic morphology of layers of both materials shows a dependence on substrate temperature, which is much more pronounced in case of HfO_2.

Raman spectra of the films show relatively sharp phonon peaks, a single one for Pr_xO_y and a rich spectrum for HfO_2, clearly evidencing crystalline areas. This is corroborated by substrate Raman spectra which indicate a stressed interface, pointing to epitaxial Pr_xO_y and HfO_2 film growth, respectively, during the initial stages of growth.

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Keywords: High-k gate dielectric material; Praseodymium oxide; Hafnium oxide; Pulsed laser deposition

1. Introduction

According to the International Roadmap for Semiconductors [1] the thickness of the silicon dioxide gate dielectric in future Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETS) is expected to be scaled down to below 1 nm. The obtained high gate capacitance would allow higher switching frequencies of the devices at lower voltages. However, at the same time, losses due to leakage currents will increase dramatically (up to 10 A/cm^2 at 1.5 nm oxide thickness) [2]. This fundamental problem can only be solved by the substitution of the traditional SiO_2 with *high-k* dielectrics. These

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materials combine the desired high gate capacitance and low leakage because of a higher physical thickness.

The ideal replacement has not been found yet, but hafnium oxide and praseodymium oxide are promising candidates because of their high dielectric constants, $k = 20$ and 35, respectively [3], and the property of forming a smooth interface to silicon [4].

While previous investigations concentrate on standard growth methods like MBE and CVD we use pulsed laser deposition from Pr_6O_{11} and HfO_2 targets. This deposition method provides experimental simplicity and flexibility accompanied by the possibility of maintaining the target stoichiometry and using lower growth temperatures [5].

In previous experiments, we presented investigations on morphology [6], stoichiometry [7] and electrical parameters [8] of deposited Pr_xO_y layers.

In this paper, we present a comparison on pulsed laser deposited hafnium oxide and praseodymium oxide thin films on silicon(100). We concentrate on the layer morphology using optical microscopy and atomic force microscopy (AFM) and the crystalline structure of layer and interface using Raman spectroscopy.

2. Experimental

Twelve millimetres by 8 mm pieces cleaved from a p-type silicon(100) wafer (dopant density $N_A \approx 3 \times 10^{15}\ cm^{-3}$) were used as substrates. After an ex situ chemical cleaning in dilute HF and an in situ thermal processing an intense LEED pattern of the $2 \times 1/1 \times 2$ reconstructed Si(100) was achieved indicating a clean and well-ordered surface.

The dielectric films then were deposited under UHV conditions onto the directly heated substrates by ablation from sintered Pr_6O_{11} and HfO_2 targets, respectively, using the fundamental, second and third harmonic (wavelengths 1064, 532 and 355 nm) of a Nd:YAG laser at normal incidence. Using a repetition rate of 10 Hz and energy of 20 mJ/pulse an average deposition rate of 1 nm/min was achieved. During layer growth the targets were continuously scanned to avoid the formation of craters. The substrates always were oriented parallel to the targets.

AFM measurements were performed using a "Smena" microscope by NT-MDT operated in the semicontact mode. Raman spectra were measured using a Dilor XY triple spectrometer combined with an Olympus microscope. A continuous wave, diode pumped Nd:YVO_4 laser at 532 nm was used for illumination [9].

3. Results

3.1. Film morphology dependence on laser wavelength

For the investigation of the dependence of film morphology on the laser wavelength samples with a constant layer thickness, here around 10 nm, were produced by ablating the Pr_6O_{11} and HfO_2 targets with the different available harmonics of the used Nd:YAG laser at a constant fluence of about 5 J/cm^2. The thin films consist of a quite smooth background with incorporated splashes for both target materials (Fig. 1) but the number density of these splashes is higher in case of the praseodymium oxide target. Fig. 1 shows optical micrographs of Pr_xO_y (upper image) and HfO_2 (lower image) layers grown at the same conditions (room temperature, 355 nm laser wavelength). The scale for both images is given in Fig. 1b. The size of the observed splashes strongly depends on the used

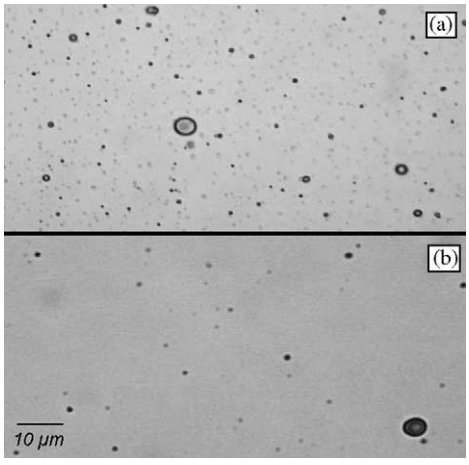

Fig. 1. Optical micrographs of 10 nm Pr_xO_y (a) and HfO_2 (b) films on Si(100) showing the typical morphology. Both films were produced using a laser wavelength of 355 nm.

Table 1
Dependence of splash diameters on laser wavelength examined by optical microscopy

Laser wavelength (nm)	Pr_xO_y/maximum diameter (μm)	Pr_xO_y/average diameter (μm)	HfO_2/maximum diameter (μm)	HfO_2/average diameter (μm)
355	3	0.6	3	0.6
532	11	1.1	5	0.7
1064	15	1.3	7	1.0

laser wavelength. Evaluating the data given in Table 1, a similar tendency for praseodymium oxide as well as for hafnium oxide is found: the diameter of the observed splashes scales inversely with the applied photon energy. Hereby, the average diameter increases from 0.6 (355 nm laser wavelength) to 1.3 μm (1064 nm laser wavelength) for Pr_xO_y and from 0.6 to 1.0 μm for HfO_2. The data given were determined by counting and measuring the splashes visible on optical micrographs and thus are limited to features bigger than 0.5 μm.

The origin of splashes is not fully understood yet, but qualitatively the tendency for their appearance can be described using a non-dimensional absorption parameter [10]:

$$B = \frac{\alpha}{I(1-R)} \frac{D_{\mathrm{th}} H_{\mathrm{v}}}{\gamma} \quad (1)$$

Eq. (1) gives a relationship between optical parameters of the material and the laser (absorption coefficient α, reflectivity R, intensity I), thermal properties of the material (thermal diffusion length D_{th}, latent heat of evaporation H_{v}, ratio of specific heats γ) and the tendency to produce splashes. Hereby, a larger parameter B means a lower tendency. Comparing the parameter for one material and different wavelengths one finds a good agreement with the experimental data: since the used photon energies (ranging from 1.2 to 3.5 eV) are lower than the bandgap of the materials (around 3.5 and 5.5 eV for Pr_xO_y and HfO_2, respectively [3,11]) the first factor, and thus the product, increases with decreasing wavelength. A comparison between the B-parameters when using different materials is quite difficult due to hardly accessible thermal property data.

3.2. Film morphology dependence on substrate temperature

While an optical microscope is limited to a lateral resolution of about 0.5 μm, an AFM allows investigating morphology on a nanometer scale. For this purpose, 10 nm thick layers of HfO_2 and Pr_xO_y were deposited on silicon at substrate temperatures ranging from room temperature to 900 °C. For all samples, the laser parameters were kept at 355 nm wavelength and 20 mJ pulse energy. Fig. 2 shows topography images (upper image: HfO_2, lower image: Pr_xO_y) of layers grown at 650 °C substrate temperature. The films of both materials seem to consist of grains with an average diameter of around 40 nm and an average height of around 2 nm. In addition to this, the hafnium oxide film is not as smooth as the praseodymium oxide film, exhibiting holes and some bigger features on top of the actual layer. These larger features exhibit the same lateral size but appear to be much higher (8 nm). Moreover, they seem to be aligned to Si[011] and Si[01 −1] since the edges of the cleaved substrates were rotated by 45° with reference to the scan direction of the AFM (left to right for all images shown).

It should be noted that there are only slight changes in morphology for both materials when using substrate temperatures below 650 °C. Namely the roughness increases from 0.26 to 0.85 nm for Pr_xO_y and from 0.49 to 0.89 nm for HfO_2. The reason for this is an increase in height of the observed crystallites.

If the substrate temperature is increased up to 900 °C dramatic changes in morphology can be observed (Fig. 3). In case of hafnium oxide (upper image in Fig. 3), the holes mentioned before increase in lateral size drastically from 100 to 700 nm and extend deep into the substrate (around 300 nm), indicating an aggressive etching of the silicon. In addition to this thermal instability of the HfO_2/Si interface ordered structures appear. There are two typical shapes: rod-like crystallites with edges parallel to Si[011] and Si[01 −1] and a typical size of 40 μm × 80 μm and larger, plane areas. To make clear the described features, a topography image with higher resolution is shown in Fig. 4.

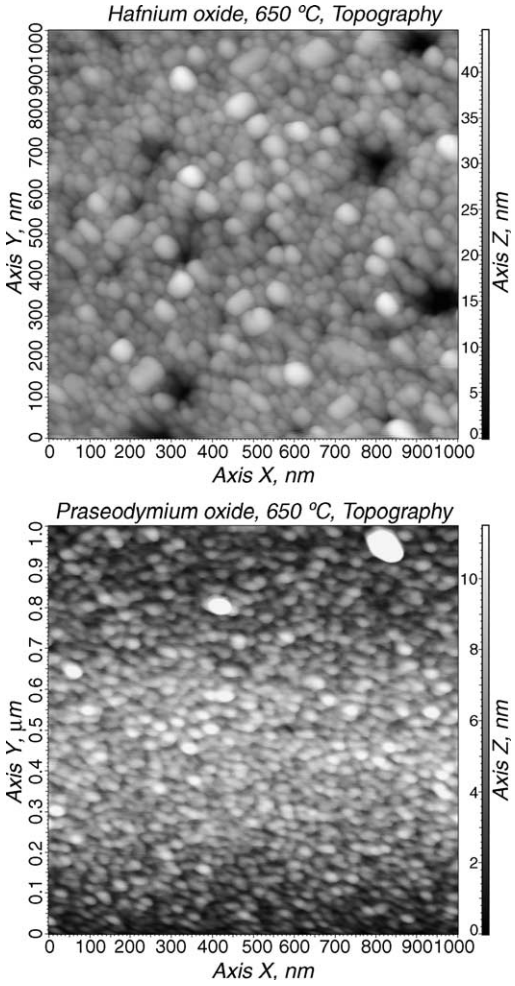

Fig. 2. AFM topography images of 10 nm thick HfO_2 (top) and Pr_xO_y (bottom) films grown at 650 °C on Si(100). There are three features visible: small islands with a lateral size of around 40 nm in the background, bigger island with a size of 50 nm in the foreground and deep holes reaching the substrate. Note the change in amplitude by a factor of 4.

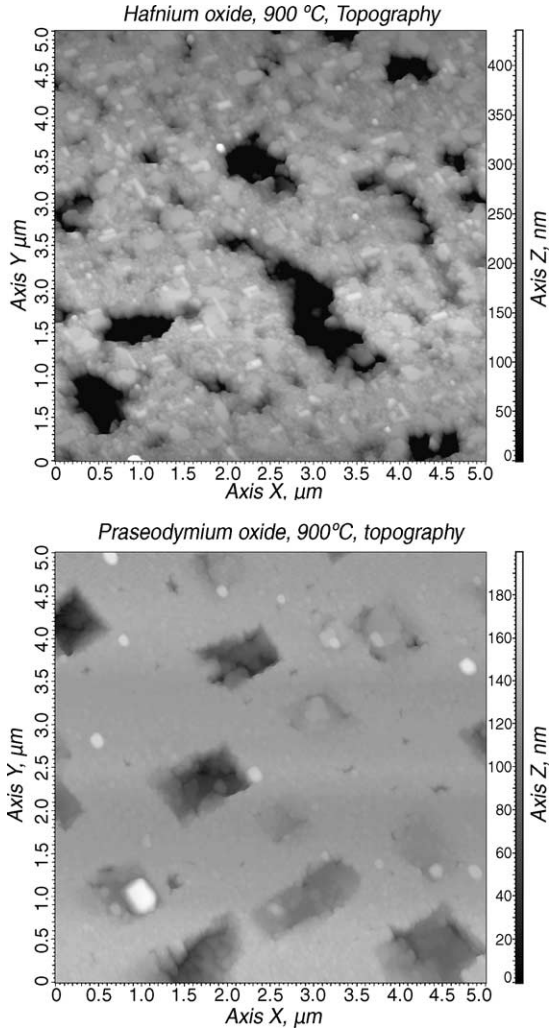

Fig. 3. AFM topography images of 10 nm thick HfO_2 (top) and Pr_xO_y (bottom) films grown at 900 °C on Si(100). On HfO_2 angular areas appear, indicating the formation of crystallites.

For Pr_xO_y (lower image in Fig. 3), there is also an etching but the resulting pits are regular and parallel to the Si[011] and Si[01 −1]. So, taking into account the lower depth of the pits (around 100 nm), the erosion seems to be slower and perhaps has a different chemical background. The area between the etch pits does not change in comparison with samples grown at 650 °C substrate temperature: still there are grains with a typical diameter of 50 nm.

The differences in evolution of morphological features for the investigated materials may be explained by a different chemical behaviour of the oxides in contact with silicon. While for Pr_xO_y a silicate is formed at the interface [4,7], HfO_2 is known for forming SiO_2. The silicon dioxide partially decomposes into silicon monoxide, which is volatile [12]. For the samples grown at 900 °C substrate temperature silicides were found for both materials by X-ray photoemission spectroscopy but the fraction is much higher for hafnium [13]. For this reason, we

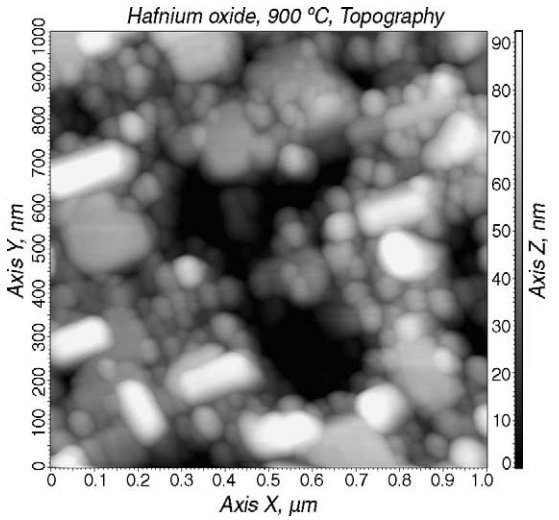

Fig. 4. Enlarged view of HfO_2 layer grown at 900 °C substrate temperature.

suggest that at least some of the crystalline areas on the hafnium oxide samples consist of hafnium silicide.

3.3. Crystalline structure of layers and interfaces

To get further information about the crystalline structure of the produced layers and the interface to the silicon substrate μ-Raman spectroscopy with a lateral resolution of about 1 μm was applied. Also, the stress at the interface to the silicon substrate was determined.

Experiments on Pr_xO_y/Si structures published before [6] showed two phases of praseodymium oxide. One of them is characterized by narrow and intense Pr-Raman signals indicating crystalline layer quality. The other one displays a very broad signal and thus may be attributed to an amorphous or polycrystalline phase. We have strong indication that the crystalline signal originates mainly from the splashes and the amorphous signal is associated with grainy background observed with AFM. Very interesting is a detailed analysis of the residual silicon phonon signal. It is shifted toward higher wave numbers by 0.32 cm^{-1} indicating compressive stress at the interface. This stress arises from oxygen-rich praseodymium oxide with a slightly lower lattice constant than silicon [6,14].

In case of hafnium oxide, the Raman spectrum consists of a high number of phonon peaks as shown in

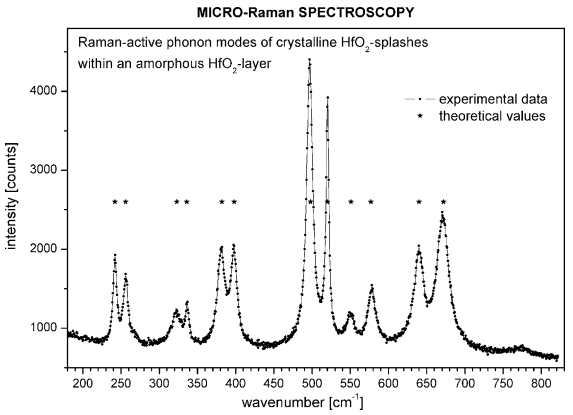

Fig. 5. Raman spectrum of a splash within a hafnium oxide layer. The very narrow and well-defined peaks indicate a good crystalline quality. Experimental results are in excellent agreement with theoretical values [15].

Fig. 5. The Raman data were taken of splashes, which were incorporated in the growing layer. Remarkably, the recorded phonon modes agree very well with theoretical values for crystalline HfO_2 reported in [15]. Outside of the splashes no Raman signal could be recorded. This fact suggests again an amorphous or polycrystalline structure of the films.

Comparing the silicon phonon peak positions measured on an uncovered site on the samples and underneath the hafnium oxide layers a shift towards lower wave numbers is observed. This shift indicates, in contradiction to Pr_xO_y, a tensile stress at the interface. The origin of this is not fully understood yet.

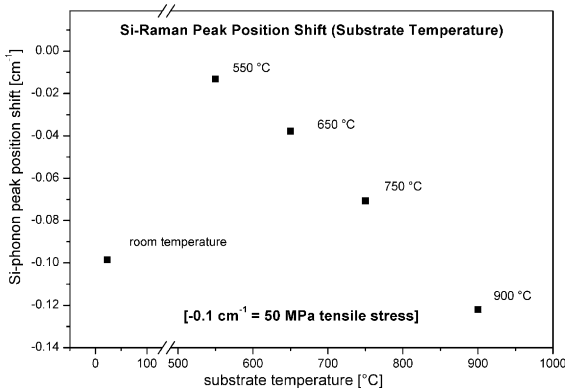

Fig. 6. Silicon Raman peak shift in dependence of growth temperature. All measurements indicate tensile stress while the magnitude of this stress changes with growth temperature.

The magnitude of the silicon phonon peak shift changes for layers grown at different temperatures from 0.12 to 0.02 cm^{-1} as shown in Fig. 6. When increasing the substrate temperature from room temperature to 650 °C the stress at the interface is decreased by a factor of 5. If the temperature is increased further up to 900 °C the stress increases again, almost linearly with temperature, and reaches a slightly higher value compared with layers grown at RT. A possible explanation for this behaviour would be the competition of two processes: a higher crystalline quality of the hafnium oxide layer near the interface due to elevated temperatures and the growth of an interfacial SiO_2 layer of different thicknesses. The first process would encourage a crystalline growth at the interface and thus lowers the stress while the second process, accompanied by the general roughening of the interface, increases the observed stress [16].

4. Conclusions

The reported results show the possibility of preparing thin dielectric films on silicon substrates by pulsed laser deposition. The investigated materials, praseodymium oxide and hafnium oxide, show different behaviours regarding film morphology, crystalline quality and influence on the substrate.

Unlike praseodymium oxide, hafnium oxide exhibits a lower tendency for producing splashes. When grown at room temperature both oxides form layers consisting of grains with a lateral dimension of about 40 nm. If the substrate temperature is increased these structures appear to be stable in case of Pr_xO_y layers. For HfO_2, there is strong indication of recrystallization. For elevated temperatures, an etching of the silicon substrate could be observed for both materials but the effect is more enhanced for hafnium oxide.

Raman stress measurements show different stresses applied to the substrate, compressive stress for Pr_xO_y and tensile stress for HfO_2. A pronounced temperature dependence of the observed stress in case of hafnium oxide layers indicates the competition of epitaxial growth and the formation of interfacial silicon oxide.

Acknowledgements

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References

[1] The International, Technology Roadmap for Semiconductors, Semiconductor Industry Association, 2001, for most recent update see http://public.itrs.net.
[2] M. Buchanan, IBM J. Res. Develop. 43 (1999) 245.
[3] G.D. Wilk, R.M. Wallace, J.M. Anthony, J. Appl. Phys. 89 (2001) 5243.
[4] A. Fissel, J. Dabrowski, H.J. Osten, J. Appl. Phys. 91 (2002) 8986.
[5] D.B. Chrisey, G.K. Hubler, Pulsed Laser Deposition of Thin Films, John Wiley & Sons, New York, 1994.
[6] D. Wolfframm, M. Ratzke, S. Kouteva-Arguirova, J. Reif, Mat. Sci. Semicond. Proc. 5 (2003) 429.
[7] D. Wolfframm, M. Ratzke, M. Kappa, M.J. Montenegro, M. Döbeli, Th. Lippert, J. Reif, Mat. Sci. Eng. B 109 (2004) 24.
[8] M. Ratzke, D. Wolfframm, T. Arguirov, M. Kappa, J. Reif, Appl. Phys. A 79 (2004) 1249.
[9] S. Kouteva-Arguirova, T. Arguirov, D. Wolfframm, J. Reif, J. Appl. Phys. 94 (2003) 4946.
[10] L.C. Chen, Pulsed Laser Deposition of Thin Films, John Wiley & Sons, New York, 1994.
[11] H.J. Osten, J.P. Liu, H.J. Müssig, Appl. Phys. Lett. 80 (2002) 297.
[12] S. Sayan, E. Garfunkel, J. Appl. Phys. 94 (2003) 928.
[13] M. Kappa, M. Ratzke, D. Wolfframm, J. Reif, to be published.
[14] H.J. Müssig, J. Dabrowski, K. Ignatovich, J.P. Liu, V. Zavodinsky, H.J. Osten, Surf. Sci. 504 (2002) 159.
[15] H. Arashi, J. Am. Ceram. Soc. 75 (1992) 844.
[16] D.J. Olego, H. Baumgart, G.K. Celler, Appl. Phys. Lett. 52 (1988) 483.