Semiconductor nanocrystals in dielectrics for memory purposes

Summary of the Ph.D. thesis

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Introduction

Semiconductor non-volatile memories (used e.g., in memory cards and in solid-states drives) are indispensable parts of everyday life. Their technological aspects for sustainable developments require new structures and new solutions for device operation. The use of semiconductor (mostly Si and Ge) nanocrystals embedded in a dielectric layer for the charge storage medium is a promiseful new way for achieving low programming voltages and reliable devices. Despite the recent promising developments, there is still much to be learned about the physics of charge tunneling and storage processes, such as the transport mechanism and storage of charge carriers in the presence of nanocrystals. The dielectric layer with embedded nanocrystals itself is an interesting new topic for structural investigations, e.g., for the construction of new adequate models for spectroscopic ellipsometry.

Objectives

The main objective of my Ph.D. work was the experimental study of the preparation and operation of metal–insulator–semiconductor (MIS) capacitance structures with embedded Si or Ge nanocrystals. The preparation of such structures involved low-pressure chemical vapor deposition, electron beam evaporation and nitric acid oxidation (the latter was applied to Si nanocrystals for the first time). The size, density and location of these nanocrystals was varied to optimize the memory properties (charge injection and charge storage). Size-dependent structural parameters of the nanocrystalline structures (mainly the nanocrystal size, density and separation, and the thin film thickness and composition) were determined by a variety of investigation methods, such as spectroscopic ellipsometry, cross-sectional transmission electron microscopy (XTEM), atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy, and sheet resistance measurements.

Intensive research in recent years enabled the embedded nanocrystal structures to become suitable for the low charging voltage needs (below 10 V) of the non-volatile industry. However, numerous physical aspects of the device operation is still not clear: e.g., whether the charge is stored in quantum states of a nanocrystal quantum box or in defect states at the nanocrystal/dielectric interface. There is only scant data about the charge distribution in the layer in the presence of nanocrystals as well. My contribution to the topic was, on one hand, the electrical memory investigation of such structures, as a function of structural parameters of the embedding layers and the nanocrystals, and on the other hand, the structural investigations of nanomaterial systems, which itself bears also important challenges. For example, the absence of reference dielectric spectra for the optical models of nanocrystalline materials is a considerable deficiency. That is why spectroscopic ellipsometry was applied for the parametric composition of the dielectric function of nanocrystalline silicon.

Experimental methods

Si and Ge nanocrystals (with sizes between 2–20 nm and 6–15 nm, respectively) embedded in Si_3N_4, in SiO_2 and in Si_3N_4/SiO_2 thin layers on top of Si substrates were prepared in MFA. Most of the structural investigations (including XTEM, AFM, SEM, and spectroscopic ellipsometry) were performed also in MFA. The memory characterization (including the memory window and charge retention measurements) of the contacted samples were performed with a method based on my own development. During these room-temperature measurements, the amplitude of the charging voltage pulses was varied between ±2–20 V, and their duration between 1–1000 ms.

New scientific results

1. I have determined a systematic dependence of the Si distribution as a function of high-temperature annealing time in low-pressure chemical vapor deposited SiN_x/nc-Si/SiN_x structures prepared on Si wafers, by spectroscopic ellipsometry. The Si content decreased in the top layer and increased in the bottom layer due to annealing [6,7]. The increase of the Si content in the bottom layer is confirmed by X-ray photoelectron spectroscopy results [10,11]. This indicates the diffusion of Si atoms from the top to the bottom SiN_x layer, through the grain boundaries of the middle nanocrystalline Si layer. During the annealing steps, the middle nanocrystalline Si layer exhibited an increase of the nanocrystal size, as revealed by both ellipsometry and cross-sectional transmission electron microscopy [6,7]. I have observed similar diffusion phenomenon was detected for different structures (Ge-rich SiO_2 layers on top of Si) [4,5].

2. Studying Si_3N_4/nc-Si/Si_3N_4 structures prepared on Si wafers by spectroscopic ellipsometry I have determined that selected oscillator parameters of Adachi's Model Dielectric Function (the strength and broadening parameter of the Damped Harmonic Oscillator at 4.24 eV, and the broadening parameter of all Critical Points at 3.31 eV) exhibited correlation with the nanocrystal size. The transition of the dielectric function of the nanocrystalline Si layer from large nanocrystals to smaller nanocrystals was agreeable to the transition of the dielectric function of reference materials with different crystallinity from the crystalline to the amorphous phase. [3]

3. I have identified the Volmer-Weber type of nanocrystal growth mechanism in the case of electron-beam evaporated Ge nanocrystals on top of SiO_2 covered Si wafers based on the size and density of Ge nanocrystals obtained by atomic force microscopy and scanning electron microscopy. I have determined a systematic dependence between the sheet resistance and NC size. [2]

4. I have obtained that oxidation with nitric acid [8] modifies the lateral size of the Si nanocrystals in the case of low-pressure chemical vapor deposited Si nanocrystals [1,3] on Si_3N_4/nc-Si/Si_3N_4/SiO_2/Si structures, as obtained by cross-sectional transmission electron microscopy and energy-filtered cross-sectional transmission electron microscopy. I have found that the oxidation formed SiO_x between the Si nanocrystals, which increased their separation. The SiO_x was found to be present between and below the nanocrystals, and no oxygen atoms were found above the nanocrystals. This has opened the possibility to examine samples with similar lateral, but with different vertical NC size.

5. I have developed a new method for the flat-band voltage determination [1,8,9,12] for memory window and retention measurements. I have found similar charging properties for MNOS samples with different nanocrystal sizes, but with equivalent nanocrystal density. This result suggested that the density of the nanocrystals plays a key role in the charging properties of the examined samples.

   I have obtained a systematic dependence of the memory window on the nanocrystal density in both the MNS and MNOS samples [1,8], but the dependence was opposite. The explanation for this observation is based on the different distance of the NCs from the Si substrate.

Defining the relative memory window width (RMWW) as the ratio of the memory window width of a certain sample with NCs and that of its appropriate reference, I have found and explained that the RMWW increased with decreasing pulse width in most of the studied structures. I have explained the dependence of the RMWW on the charging pulse amplitude by resonant tunneling.

Utilization of the new scientific results

The results achieved by the use of spectroscopic ellipsometric measurement and evaluation led to a better understanding of the size dependence of the dielectric function of materials. The developed oxidation method for Si nanocrystals with nitric acid opened a new possibility for size modification of nanoparticles. The development of the measurement method for the flat-band voltage is exploited in the memory window and retention measurements of metal–insulator–semiconductor (MIS) memory structures. The suggested relative memory window width representation opened a new way of evaluation of experimental results, e.g., for the examination of the resonant tunneling phenomena in MIS memory structures. The obtained results on memory behavior led to a better understanding of charge injection and charge storage in MIS memory elements and to the realization of possible ways of improvement.

Until now, I have two independent citations for my publications.

Publications

This Ph.D. work is based on the following publications:

[1] P. Basa, Zs. J. Horváth, T. Jászi, A. E. Pap, L. Dobos, B. Pécz, L. Tóth, and P. Szöllősi, *Electrical and memory properties of silicon nitride structures with embedded Si nanocrystals*, Physica E **38**, 71–75 (2007) (Impact factor in 2006: 1.084)

[2] P. Basa, G. Molnár, L. Dobos, B. Pécz, L. Tóth, A. L. Tóth, A. A. Koós, L. Dózsa, Á. Nemcsics, and Zs. J. Horváth, *Formation of Ge nanocrystals in SiO_2 by electron beam evaporation*, Journal of Nanoscience and Nanotechnology **8**, 818–822 (2008) (Impact factor in 2006: 2.194)

[3] P. Basa, P. Petrik, M. Fried, L. Dobos, B. Pécz, L. Tóth, *Si nanocrystals in silicon nitride: an ellipsometric study using parametric semiconductor models*, Physica E **38**, 76–79 (2007) (Impact factor in 2006: 1.084)

[4] P. Basa, A. S. Alagoz, T. Lohner, M. Kulakci, R. Turan, K. Nagy, Zs.J. Horváth, *Electrical and ellipsometry study of sputtered SiO_2 structures with embedded Ge nanocrystals*, Applied Surface Science **254**, 3626–3629 (2008) (Impact factor in 2006: 1.436)

[5] P. Basa, P. Petrik, M. Fried, A. Dâna, A. Aydinli, S. Foss, T. G. Finstad, *Spectroscopic ellipsometric study of Ge nanocrystals embedded in SiO_2 using parametric models*, Physica Status Solidi C **5**, 1332–1336 (2008)

[6] P. Basa and P. Petrik, *SiN_x/nc-Si/SiN_x multilayers: a spectroscopic ellipsometric study*, Romanian Journal of Information Science and Technology **8**, 235–240 (2005)

[7] Zs. J. Horváth, P. Basa, P. Petrik, Cs. Dücső, T. Jászi, L. Dobos, L. Tóth, T. Lohner, B. Pécz, and M. Fried, *Si nanocrystals in sandwiched SiN_x structures*, Proceedings of the First International Workshop on Semiconductor Nanocrystals, SEMINANO2005, Volume 2, 417–420 (2005)

[8] Zs. J. Horváth, P. Basa, T. Jászi, A. E. Pap, L. Dobos, B. Pécz, L. Tóth, P. Szöllősi, and K. Nagy, *Electrical and memory properties of Si_3N_4 MIS structures with embedded Si nanocrystals*, Journal of Nanoscience and Nanotechnology **8**, 812–817 (2008)
(Impact factor in 2006: 2.194)

[9] P. Szöllősi, P. Basa, Cs. Dücső, B. Máté, M. Ádám, T. Lohner, P. Petrik, B. Pécz, L. Tóth, L. Dobos, L. Dózsa, and Zs. J. Horváth, *Electrical and optical properties of Si-rich SiN_x layers: Effect of annealing*, Current Applied Physics **6**,
179–181 (2006) (Impact factor in 2006: 1.184)

[10] D. L. Wainstein, A. I. Kovalev, Cs. Dücső, T. Jászi, P. Basa, Zs. J. Horváth, T. Lohner and P. Petrik, *X-ray photoelectron spectroscopy investigations of Si in non-stoichiometric SiN_x LPCVD multilayered coatings*, Physica E **38**, 156–159 (2007)
(Impact factor in 2006: 1.084)

[11] A. I. Kovalev, D. L. Wainstein, D. I. Tetelbaum, A. N. Mikhailov, Y. Golan, Y. Lifshitz, A. Berman, P. Basa, Zs. J. Horvath, *Electron spectroscopy investigations of semiconductor nanocrystals formed by various technologies*, International Journal of Nanoparticles **1**,
14–31 (2008)

[12] Basa P., Horváth Zs. J., Jászi T., Molnár G., Pap A. E., Dobos L., Tóth L., Pécz B.: *Nem-illékony nanokristályos félvezető memóriák*, Híradástechnika **62**, 43–46 (2007)

Other publications related to the subject:

[13] P. Petrik, M. Fried, T. Lohner, N. Q. Khánh, P. Basa, O. Polgár, C. Major, J. Gyulai, F. Cayrel and D. Alquier, *Dielectric function of disorder in high-fluence helium-implanted silicon*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms **253**, 192–195 (2006) (Impact factor in 2005: 1.181)

[14] P. Petrik, M. Fried, É. Vázsonyi, T. Lohner, E. Horváth, O. Polgár, P. Basa, I. Bársony and J. Gyulai, *Ellipsometric characterization of nanocrystals in porous silicon*, Applied Surface Science **253**, 200–203 (2006) (Impact factor in 2005: 1.263)