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STUDY OF Ge NANODOTS EMBEDED IN AMORPHOUS SiO_2

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Outline:

- ✓ Preparation and measurements
- ✓ TEM investigations
- ✓ XPS investigations
- ✓ Conclusions

✓ **Preparation and measurements**

Preparation methods:

- sol-gel:
  - ❖GeCl4, TEOS (tetraethyl orthosilicate) precursors in ethanol;
  - ❖Ge/Si molar ratio was varied between 3 % and 12 %
  - ❖deposition : spinning coating method
  - ❖heating in air at 500 – 600 ^{o}C (after drying)
  - ❖Annealing in N_2 (1 atm and 800 ^{o}C) or H_2 (2 atm and 500 ^{o}C)

- radio frequency magnetron sputtering:
  - ❖150 W RF constant power, argon pressure
  - ❖0.3 Pa.,1.78 MHz generator for 1h
  - ❖Ge/Si molar ratio 40 % in the GeSiO films
  - ❖Annealing in H_2 (2 atm and 500 ^{o}C)

Measurements: TEM, SAED, EDX, XPS

TEM: preparation of specimens

- ❖ cross section method and ion milling – sol-gel films (~280 nm)
- ❖ extraction - scratching the film surface with a thin diamond tip – sputtered films (~1500 nm)

XPS analysis:

- ❖ excited with unmonochromatized Al Ka (1486.61 eV) radiation and monochromatized Ag La (2984.3 eV) radiation

✓ TEM investigations

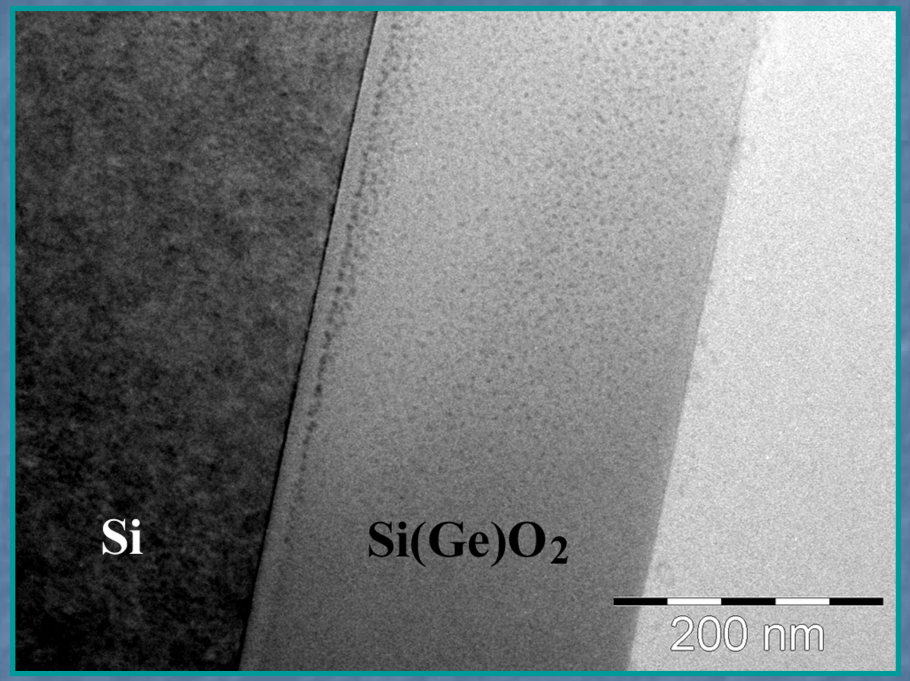


Fig. 1. Low magnification XTEM image of sol-gel film annealed in N_2

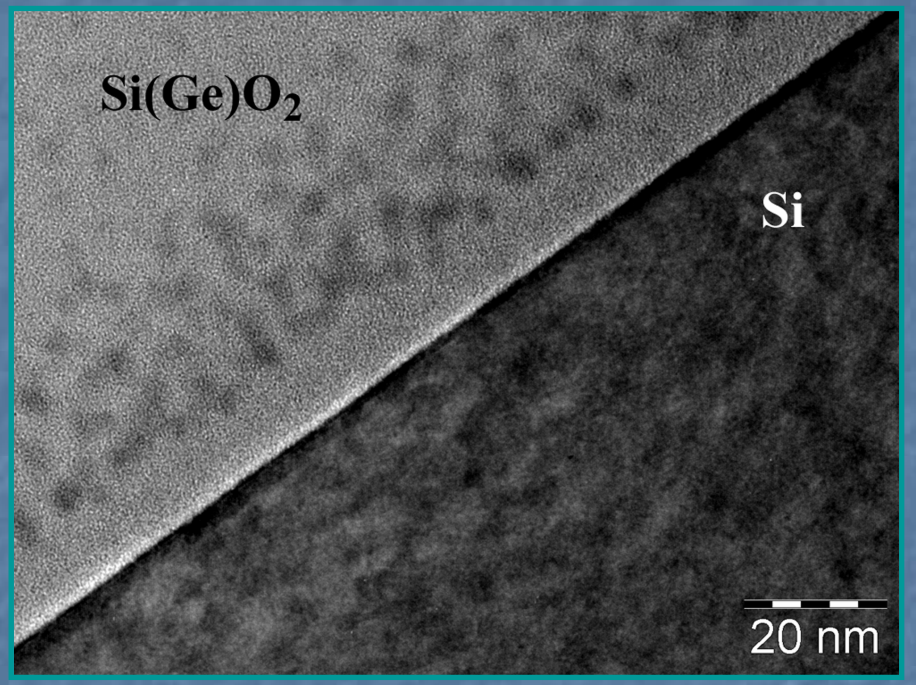


Fig. 2. Interface region of the silicon substrate with the GeSiO sol-gel film annealed in N_2. A 10 nm layer without nanodots appears at the interface

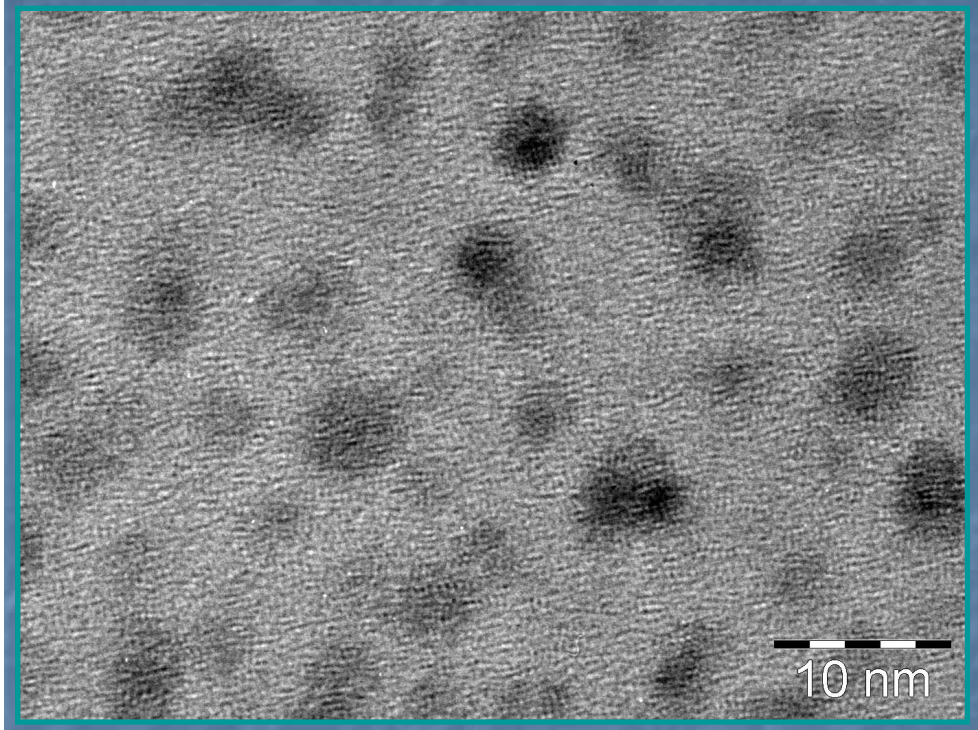


Fig. 3. Detail of the XTEM image in the midst of the film thickness: globular amorphous nanodots rich in Ge in contrast with the SiO_2 matrix.

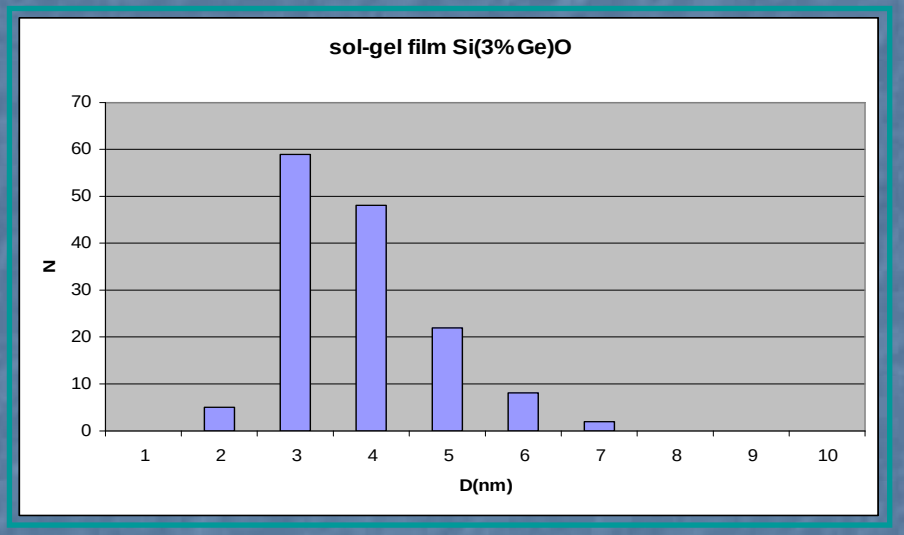


Fig. 4. Size distribution (3 - 6 nm) of the rich Ge nanodots in the SiO_2 matrix. Average size: 3.8 nm.

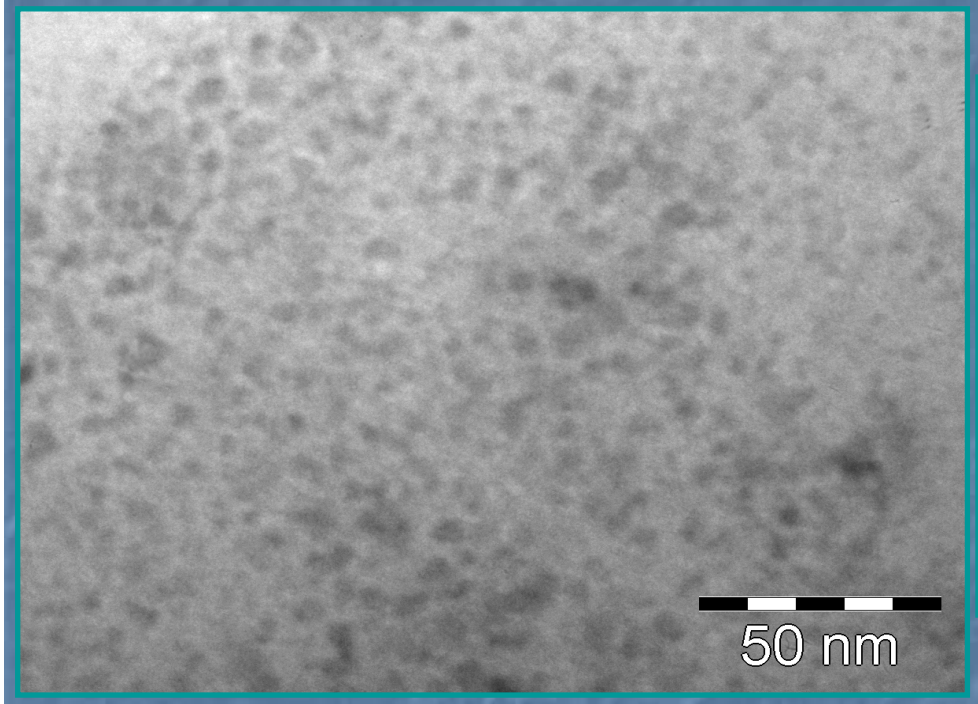


Fig. 5. Plan view TEM image of the Si(12 % Ge)O sol-gel film annealed in H_2.

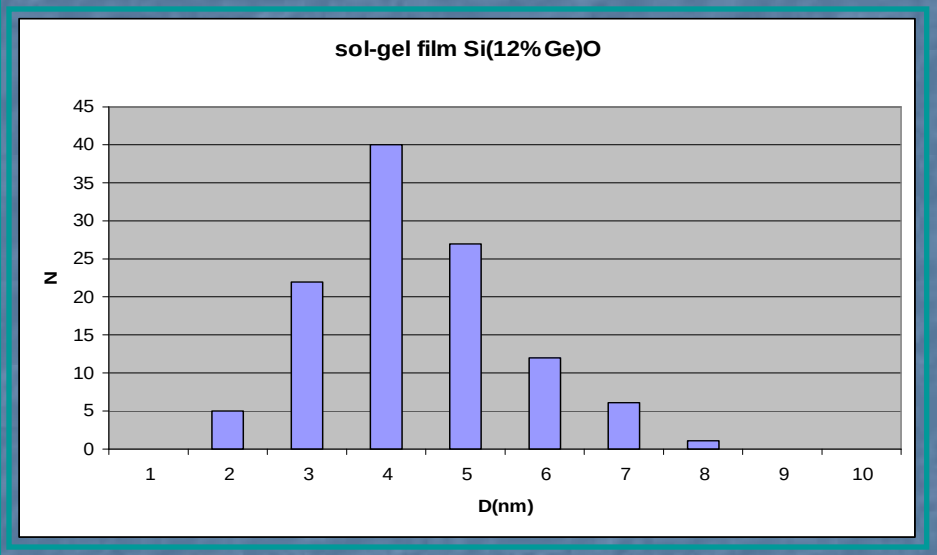


Fig. 6. Distribution of the nanodots in the Si(12 % Ge)O sol-gel film. Average size: 4.3 nm

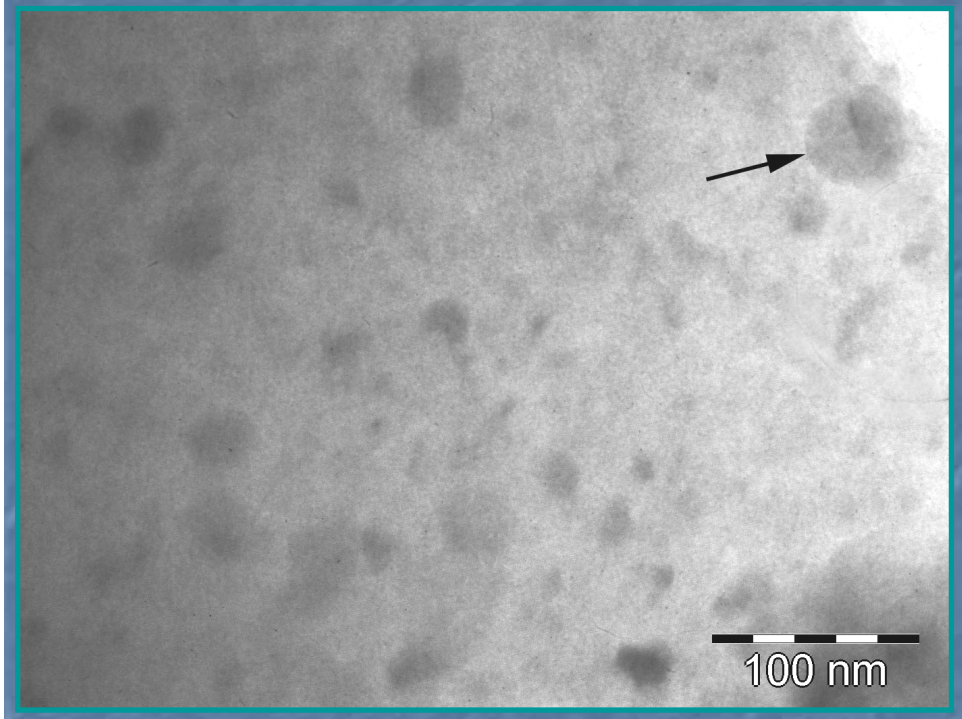


Fig. 7. Plan view TEM image of a fragment from the sputtered film

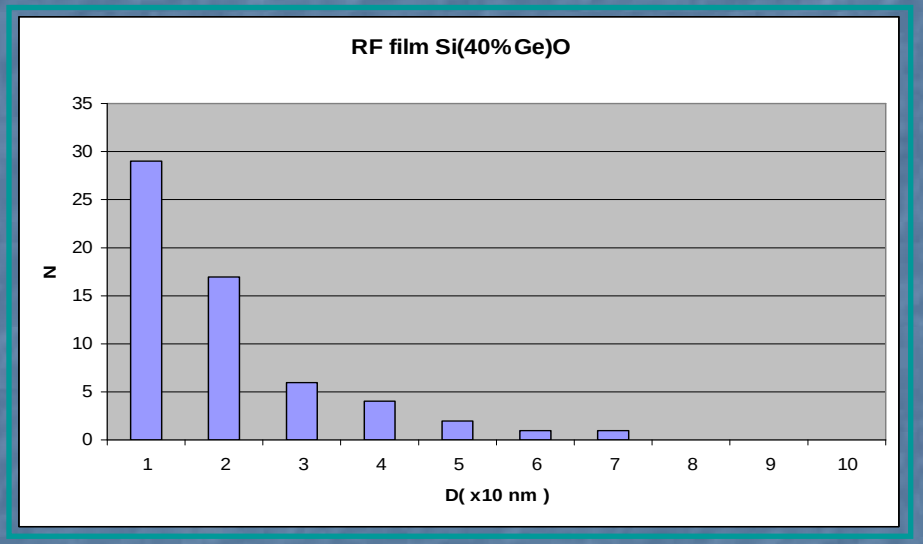


Fig. 8. Size distribution of the particles in the sputtered film. Average size: 20 nm

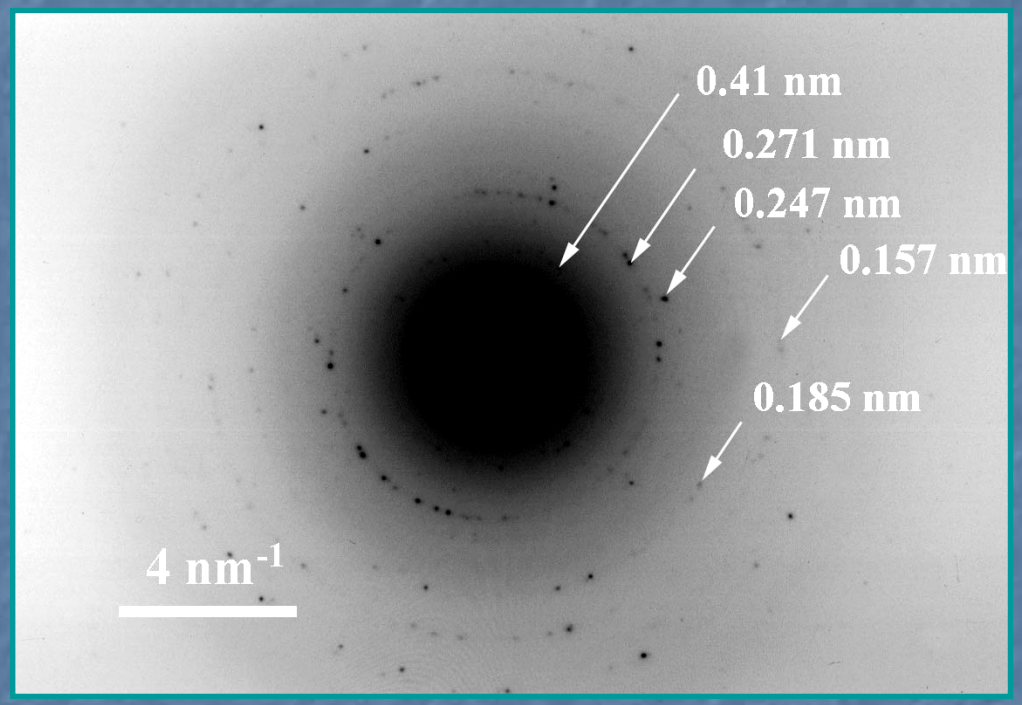
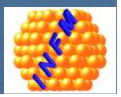


Fig. 9. SAED pattern of the sputtered film. Strong diffraction spots are distributed in a clear ring (lattice distance: 0.271 nm). Main contribution from crystalline nanodots larger than 50 nm

Table I. SAED experimental measurements and the possible crystalline structures expected for the Ge precipitate in amorphous SiO_2 matrix

GeO PDF nr: 30-0590	Ge PDF nr: 51-0767	Ge Tetragonal PDF nr: 18-0549	Ge Cubic PDF nr: 04-0545	Experimental measurements SAED pattern in fig 9
nonindexed	a = 0.962 nm c = 0.578 nm	a = 0.593 nm c = 0.698 nm	a = 0.5657	
d(nm) (hkl) Inten.	d(nm) (hkl) Inten.	d(nm) (hkl) Inten.	d(nm) (hkl) Inten.	d(nm) eror. Relative Inten.
0.502 nm 60 0.430 nm 40 0.347 nm 60 0.325 nm 60 0.305 nm 100 **0.270 nm 100** 0,262 nm 60	0.3650 (111) 12 0.3131 (210) 24 **0.2734 (012) 100** 0.2475 (112) 4 0.2316 (310) 19 **0.1847 (222) 81** **0.180 (312) 59** 0.1754 (203) 61	0.452 (101) 6 0.359 (111) 16 0.301 (102) 40 **0.2728 (201) 100** 0.268 (112) 20 0,2478 (211) 16 **0.187 (310) 20** **0.1829 (203) 20** 0.181 (311) 20	0.3266 (111) 100 0.2000 (220) 57 0.1706 (311) 39 0.1414 (400) 4 0.12980 (331) 10	0.411 +/- 0.002 nm small 0.389 +/- 0.002 nm small **0.271 +/- 0.001nm strong** 0.247 +/- 0.001nm strong 0.238 +/- 0.002nm small **0.185 +/- 0.001nm medium** 0.157 +/-0.001 nm medium 0.133 +/- 0.001 nm small



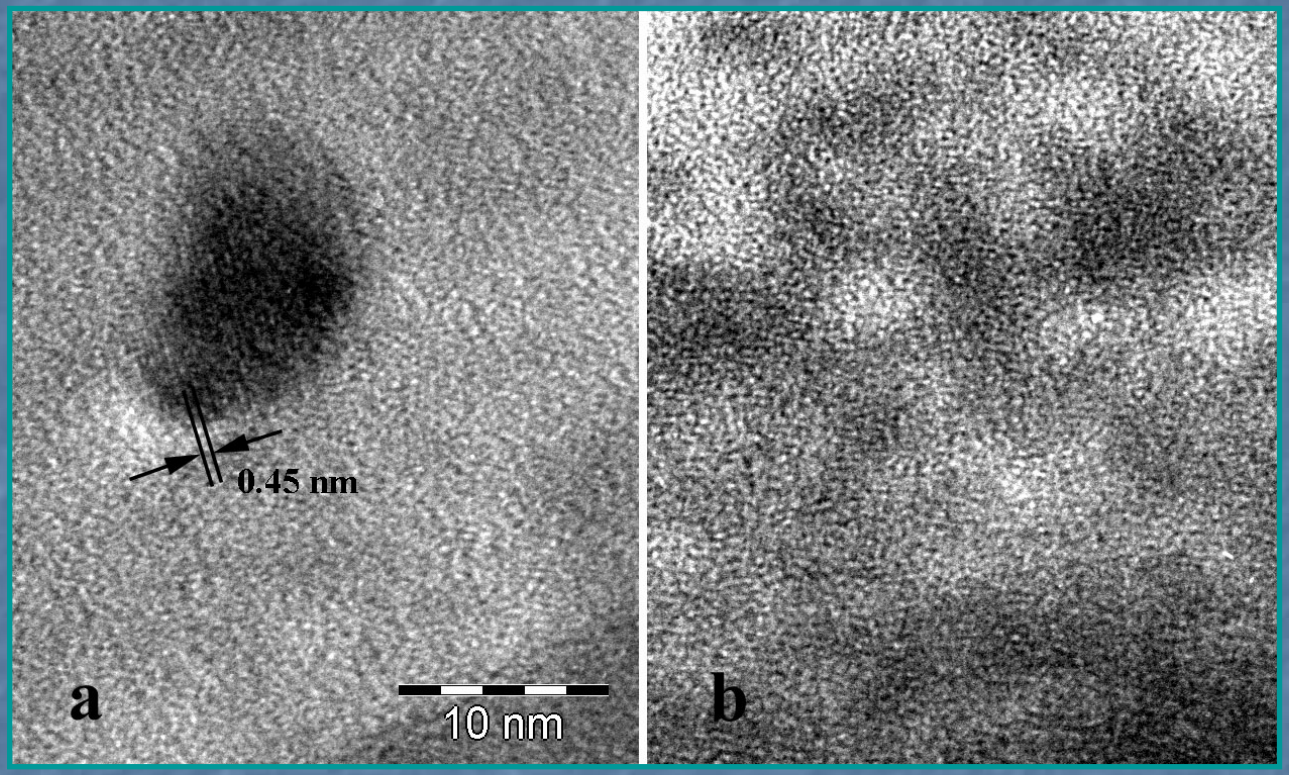


Fig. 10. HRTEM images of the sputtered film.
A – crystallized Ge nanodot lattice interfanges correspond to tetragonal phase
B – amorphous Ge rich nanodots

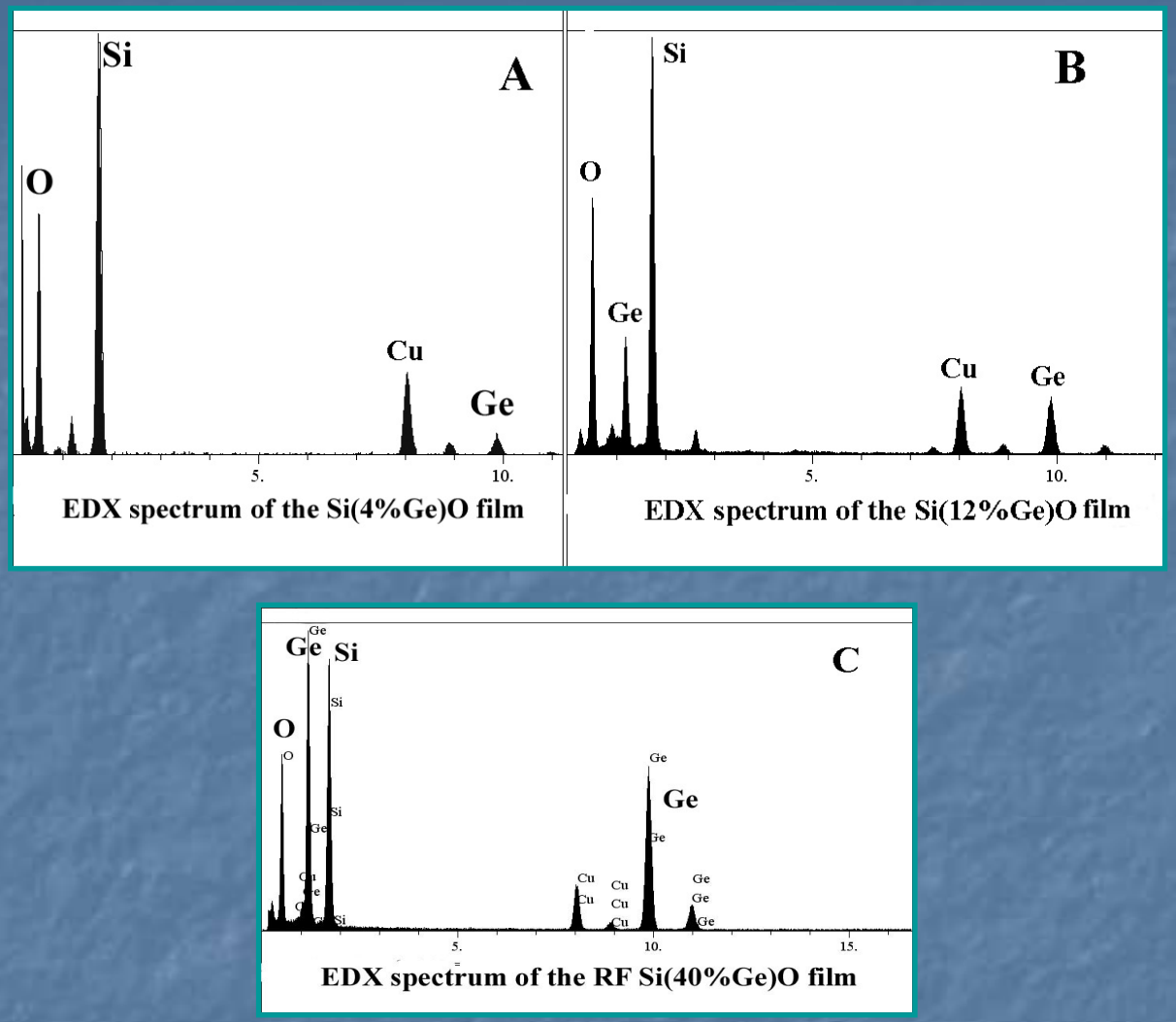


Fig. 11. EDX spectra of the SiGeO films. A – spectrum of the SiGeO (3%Ge) sol-gel film. B – spectrum of the SiGeO (12%Ge) sol-gel film; C – spectrum of the sputtered SiGeO (40%Ge) film

✓ XPS investigations

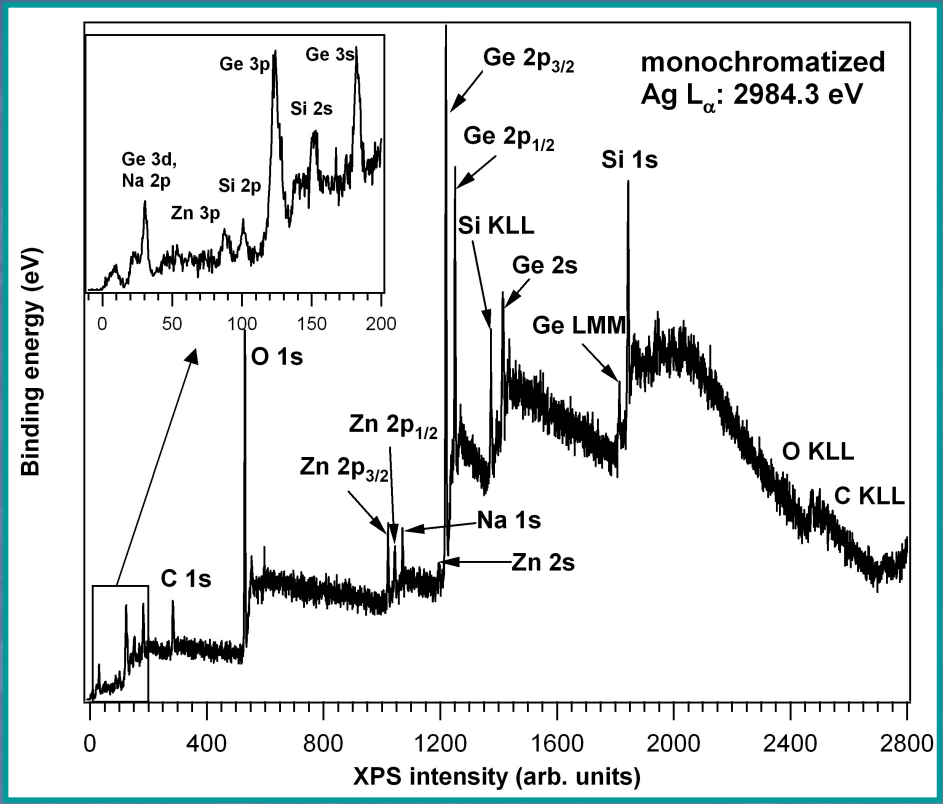


Fig. 12. Survey scan using monochromatized Ag L_α on sputtered sample.
Insert: region with binding energies lower than 200 eV.

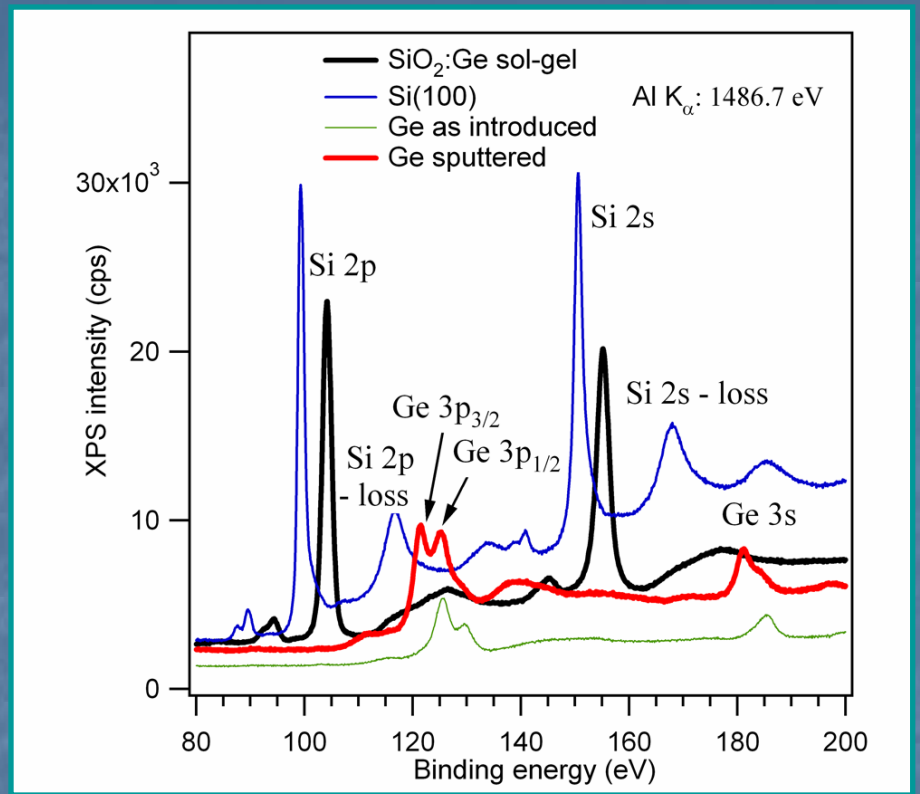


Fig. 13. Si 2p-2s and Ge 3p-3s core level spectra from a sol-gel sample;
Comparison:

- clean Si(100) sample,
- oxidized Ge
- Ge sample cleaned by ion sputtering

Table II. Si and Ge core-level positions in the various samples investigated (in bold: samples of interest), together with some references from the literature (in italic). Units: electron-volts. Typical errors: ± 0.1 eV

Core level Sample	Si 2p	Ge $3p_{3/2}$	Si 2s	Ge 3s	Ge $2p_{3/2}$
Si (001)	99.3	-	150.6	-	-
oxidized Ge crystal	-	125.6	-	185.7	1221.3
sputtered Ge crystal	-	121.5	-	181.2	1217.3
GeSiO (sol-gel)	**104.2**	**(126.2)**	**155.2**	**-**	**1221.3**
GeSiO (magnetron sputtering)	**101.6**	**123.9**	**151.2**	**181.5**	**1220.7**
Si, (Atzrodt et al. 1980)	*99.3*	-	-	-	-
Ge, (Shalvoy et al. 1977)	-	*121.2*	-	-	-
SiO_2, (Kerkhof et al. 1978)	*103.9*	-	-	-	-
SiO, (Nguyen et al. 1989)	*101.7*				
GeO_2, (Morgan et al. 1973)	-	*125.3*	-	-	-
GeO, (Morgan et al. 1973)	-	-	-	-	*1221.5*

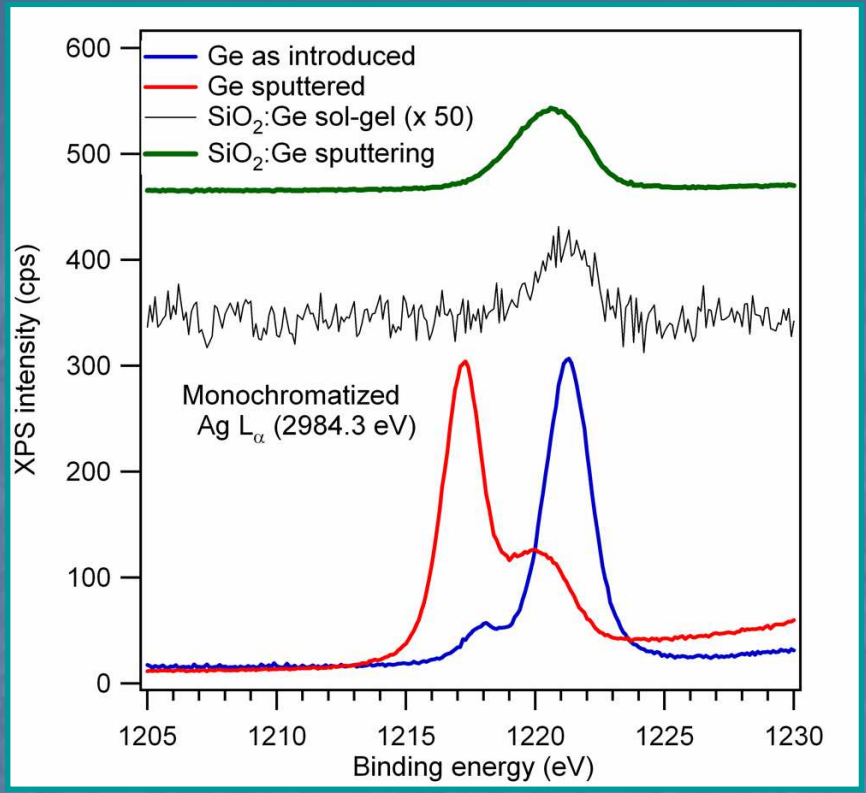


Fig. 14. Ge $2p_{3/2}$ core level (monochromatized Ag L_α source): - sol-gel sample
- sputtered sample

The spectrum of the sample prepared by magnetron sputtering was artificially shifted upwards by + 450 cps

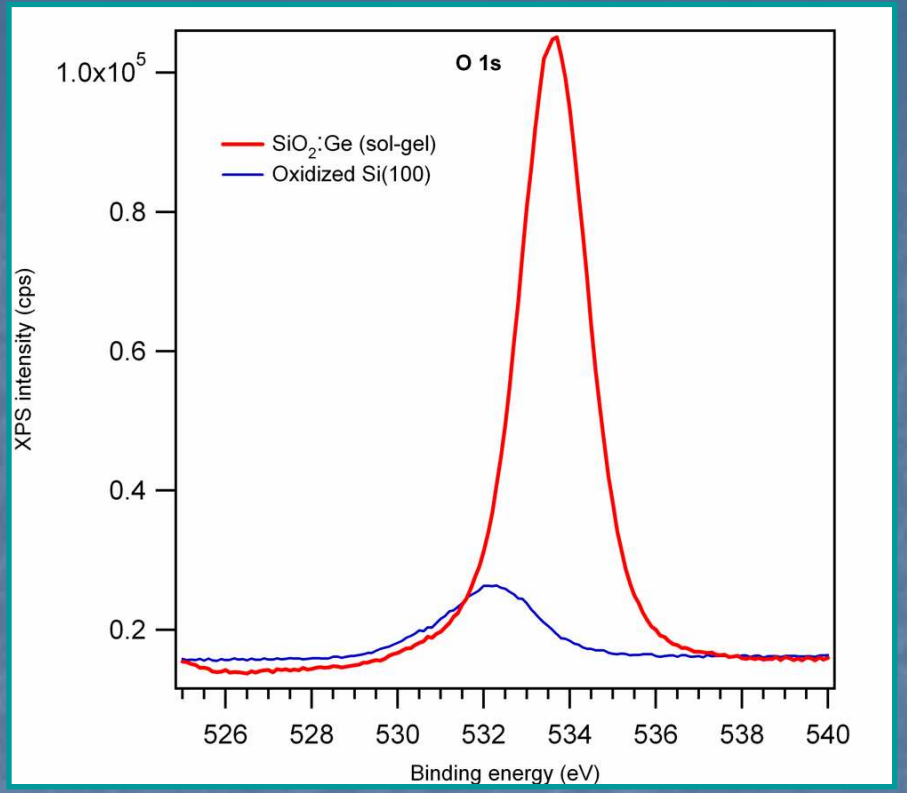


Fig. 15. O 1s core level in oxidized Si(100), as compared with the corresponding spectrum in sol-gel prepared GeSiO

Table III. Core level intensity analysis, in order to derive the Ge/Si atomic ratio in the investigated GeSiO samples

Level →	Si 2p				Ge $3p_{3/2}$				Ge $2p_{3/2}$			
Sample ↓	int.	ASF	corr.	%	int.	ASF	corr.	%	int.	ASF*	corr.	%
magn.sp.	23.5	0.25	94	25-27	113	0.4	282.5	75	76.3	0.3	254.4	73
sol-gel	91	0.25	364	94	-	0.4	-	-	1.77	0.3	5.9	6

✓ Conclusions

❖ Ge nanodots in the sol-gel films are amorphous. There average size increases with Ge concentration from 3.8 nm in GeSiO (3 % Ge) to 4.3 nm for the GeSiO (12 % Ge) films.

❖ In sputtered films (40 % Ge), two Ge different nanostructures were observed :

- ➢ crystalline tetragonal nanodots,
- ➢ a network of Ge-rich nanostructures in the amorphous silicon oxide matrix.

❖ The surface of sol-gel films: a mixture of GeO_2 and SiO_2.
The sputtered films surfaces: contain both Ge and Si suboxides.
In all cases, the Ge concentration at the surface strongly exceeds the volume concentration: (from preparation and EDX).

❖ The reduction process in the sol-gel films is mainly controlled by oxygen diffusion.

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Thank you for your attention!!!