Silicon nanocrystallites in buried SiO$_x$ layers via direct wafer bonding

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A combination of SiO vapor-deposition and direct wafer bonding is used to produce buried layers of SiO$_x$. By thermally induced decomposition, Si nanocrystals embedded in SiO$_2$ are obtained. Decomposition of the silicon suboxide is observed by studying the Si-O-Si stretching vibration in the infrared range. This phase separation process is found to start already at 400 °C and to be mostly complete after 1 h at 800 °C. Annealing at 1000 °C yields well established Si nanocrystallites of considerable density with diameters about 4 nm buried in the interface layer between the bonded silicon wafers. © 1999 American Institute of Physics. [S0003-6951(99)01831-8]

Silicon based materials consisting of nanoscale crystallites in an oxide environment exhibit unique electrical, optical, and optoelectronic properties like single electron tunneling, nonlinear optical absorption, and photoluminescence in the visible range. Such effects, closely related not only to the respective crystallite size, but also to structural characteristics and dielectric properties of the surrounding medium, have stimulated extensive studies with the ultimate goal of utilizing Si nanocrystallites for potential device applications.

Various routes of synthesis like cosputtering of Si and SiO$_2$, ion implantation of Si in SiO$_2$, reactive modes of chemical vapor deposition, laser ablation, and gas phase evaporation have been employed for the production of corresponding nanoparticulate composites.

Systematic studies on size, shape, structure as well as formation and oxidation state of Si nanocrystallites with respect to desired properties require experimental arrangements of sufficient chemical stability and mechanical robustness. For this purpose, we explored a combination of silicon direct wafer bonding, a method well suited to fabricate silicon on insulator (SOI) structures with variable parameters and properties. With the ease of SiO vapor deposition, from which Si-rich SiO$_x$ layers may readily be obtained by thermal decomposition. In this letter we report on the procedure applied to obtain SiO$_x$ layers with Si nanocrystallites buried in between two wafers, and present first results on structural and compositional characteristics of the buried layers as a function of a subsequent heat treatment. The main issue to be met with this procedure are (i) uniformity and smoothness of the layers deposited, and (ii) counterbalance of stresses induced by deposition and layer formation.

We used polished 4 in. $p$-type Si(100) wafers with no further pretreatment than cleaning by a standard RCA1 process. SiO$_x$ layers were deposited in oil-free high vacuum (2 × 10$^{-6}$ mbar) by thermal evaporation of SiO powder (BALZERS) from a Ta boat at a rate of 0.3 nm/s onto rotating substrates. The resulting layer composition achieved under these conditions was determined by Rutherford backscattering (RBS) to be of $x=1.27$, i.e., Si:O=44:56, where the slight oxygen excess is due to O$_2$ incorporation from the residual gas during deposition. By varying the deposition rate and oxygen partial pressure in the evaporation chamber, layers of different stoichiometry ranging from $x=1$ to 2 may be produced.

The SiO$_x$ layers exhibit rather smooth surfaces as required for direct wafer bonding without additional polishing. The typical microroughness as determined by atomic force microscopy (AFM) in tapping mode (Digital Instruments D 5000-1-PAL) is about 0.45 nm [root-mean-square (rms)]. Following another short RCA1 cleaning, plain wafers were bonded against the SiO$_x$ layers of the coated ones, thus producing Si-SiO$_x$-Si structures. Direct wafer bonding was carried out in a modified microcleanroom bonding machine under low vacuum (4 mbar). The obtained wafer pair had insufficient bond strength due to compressive stresses buildup in the SiO$_x$ layers which caused debonding upon thermal treatment. The residual stresses as determined by bowed measurements (Tencor FLX-2900) on 4 in. wafers with 100 nm SiO$_x$ are in the order of 350 MPa. Stress induced wafer bending was prevented by initial deposition of a SiO$_x$ counterlayer of corresponding thickness on the wafer backside, prior to deposition of the frontside layer, in order to produce a stress counterbalance.

Bonding of such wafers and annealing at 400 °C for 12 h at 2 mbar yielded the bonding strength required for cutting the wafer pair into pieces for further treatment and measurements. Such pieces of buried SiO$_x$ layers were subject to a second annealing step at 600, 800, and 1000 °C under ambient conditions for 1 h to study structural and compositional changes. After annealing at 1000 °C a final bonding strength of >13 MPa was determined by tensile strength measurement.

A second set of samples was prepared by deposition of equivalent SiO$_x$ layers on plain Si wafers for measurements that require direct access to the SiO$_x$ layer [e.g., surface roughness measurement, Fourier transform infrared (FTIR) spectroscopy]. These samples were annealed under flowing argon gas in oxygen-free environment at temperatures of 400, 600, 800, and 1000 °C for 1 h.

FTIR spectra were acquired on a Bruker IFS66v FTIR-spectrometer equipped with a mercury cadmium telluride (MCT) infrared detector. All spectra were recorded in a 90° transmission geometry on single-side polished wafers using a plain wafer piece as reference, subjected to the same anneal-

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In the 1000-1080 cm$^{-1}$ region related to the Si-O-Si stretching mode are presented in Fig. 1 for a 100-nm-thick layer. The inset of Fig. 1 shows additional features in the 3500 cm$^{-1}$ region due to adsorbed water$^{17}$ and the Si-H stretching mode around 2200 cm$^{-1}$.

According to the random bond model,$^{18}$ the structural characteristics of SiO$_x$ may be understood in terms of various Si tetrahedra with Si and oxygen atoms randomly distributed as nearest neighbor atoms. The position of the Si-O-Si stretching vibration sensitively depends on the respective annealing treatment, indicating distinct changes in the Si environment,$^{19}$ even at 400 °C. The corresponding maximum position has been previously used to calculate the composition parameter $x$ of SiO$_x$: 20

\[ x = (0.02 \times \nu) - 19.3, \]  

(1)

where $\nu$ denotes the peak maximum of the Si-O-Si stretching vibration in units of cm$^{-1}$. By thermal decomposition of SiO$_x$, a new Si phase is precipitated accompanied by an oxygen enrichment in the remaining phase. Assuming no contribution of Si precipitates to the Si-O-Si vibration and homogeneous distribution of the oxygen throughout the oxygen rich phase, the above formula can be used to calculate the composition of this phase. RBS measurements verified, that no change occurred in the overall composition of the layers during annealing.

As-deposited layers show a peak maximum at 1024 cm$^{-1}$. The calculated composition parameter $x = 1.2$ agrees fairly well with the value of $x = 1.27$ determined by RBS which indicates an almost homogeneous distribution of Si and O without noticeable precipitation. Upon annealing at 800 °C, the Si-O-Si peak is shifted to 1078 cm$^{-1}$ indicating a complete phase separation into Si and SiO$_2$ (SiO$_2$ corresponding to $\nu = 1080$ cm$^{-1}$).$^{20}$ For the layers annealed at 400 and 600 °C, composition parameters of $x = 1.48$ and 1.75, respectively, were calculated for the oxygen rich phases. The peak shift is accompanied by an increase of the peak height at the expense of the halfwidth indicative for a more narrow distribution of the various Si-O coordinations. These observations correspond to published results on the IR spectra of SiO$_x$ films prepared by different methods.$^{19-21}$

In the IR spectra of the as-deposited layers, an additional feature around 3500 cm$^{-1}$ indicates the presence of adsorbed water suggesting a certain porosity of the layer$^{17}$ (see inset of Fig. 1). Upon annealing at 400 °C, this water apparently reacts with the layer surface forming Si-H bonds which give rise to two Si-H related bands, one at 900 cm$^{-1}$ and another between 2000 and 2300 cm$^{-1}$, as reported for amorphous SiO$_x$:H.$^{20}$ With the hydrogen diffusing out at 600 °C and above these features disappear. The absence of newly adsorbed water in spectra of higher annealed samples indicates that a densification of the porous layers has occurred. A similar behavior has been reported for thin SiO$_2$ films.$^{17}$

The FTIR vibration spectroscopy studies have been complemented by high-resolution electron microscopy (HREM) studies at a JEM 4000 EX, operating at 400 kV, aimed at monitoring the formation of Si nanocrystallites upon processing the buried layers. For this purpose cross-section specimens were prepared by a combined mechanical and ion beam thinning procedure which enabled imaging of nanocrystallites from the very beginning of crystallization. No crystallization was observed at annealing temperatures up to 800 °C. While at 800 °C IR measurements suggest almost complete phase separation into Si and SiO$_2$, HREM reveals no crystallization, but a certain extent of partial ordering in the amorphous layers below the scale of crystalline transla-

FIG. 1. FTIR spectra of a 100 nm thick SiO$_x$ layer on Si, as deposited, not bonded and annealed at various temperatures. The inset shows part of the higher-wave number side of the spectra in the same order (top to bottom).

FIG. 2. HREM image of a cross-section through the two Si wafers with the buried SiO$_x$ layer in between (annealed at 1000 °C). In the higher magnified inset, Si nanocrystallites may be recognized from their lattice plane fringes.
tional order. It was only upon annealing at 1000 °C that in the 100-nm-thick buried SiO$_x$ layers distinct crystallization could be observed. The cross-sectional Fig. 2 illustrates that a rather high density of embedded Si nanocrystallites was achieved. In the inset with higher magnification, the crystallites may be recognized from their lattice plane fringes of diamond cubic (dc) type. They are uniformly distributed within the oxide layer, have approximately spherical shape, and exhibit faceting and planar lattice defects characteristic of the solid phase crystallization of dc semiconductors.$^{22,23}$ Their sizes range from about 2 to 8 nm with a mean diameter of 4.03±1.27 nm. From the dimensions of the imaged area a lower bound of 1.47×10$^{18}$ cm$^{-3}$ of the volume density of Si nanocrystallites was evaluated which corresponds to a filling factor of 6.07%.

In conclusion, buried layers of SiO$_x$ containing Si nanocrystallites have been fabricated via SiO evaporation and direct wafer bonding. Thermally induced decomposition of the oxide layers started as low as 400 °C and was mostly completed within 1 h at 800 °C. The decomposition process could be studied by the observation of the Si-O-Si stretching vibration in the FTIR spectra of the layers. For the formation of nanocrystallites, higher temperatures (1000 °C) were required. From HREM images nearly spherical shapes and narrow size distribution of the nanocrystallites having dc crystal lattice were deduced. The photoluminescence properties of these layers peaking at about 830 nm will be treated in a forthcoming letter.

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