High-resolution grazing-emission x-ray fluorescence of Mn introduced into Si from new organic precursor methods

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High-resolution grazing-emission x-ray fluorescence was used to probe the diffusion profiles of metal dopants introduced into silicon wafers through new routes exploiting the ultra-violet degradation of organometallic films. The UV degradation approach is aimed at creating ordered arrays of spin centres into a silicon matrix. The samples produced will then be exploited in quantum information processing, which relies on the interaction of spins and control atoms separated by a modelled critical distance [1]. The ability to produce regular arrays of metal dopants in semiconductors will also have profound implications in other areas of information technology and optoelectronics. In order to produce the desired doped samples, we are using manganese phthalocyanine (MnPc) molecules as a test case, which are deposited onto HF etched silicon substrates using organic molecular beam deposition (OMBD) to form 5nm thick films. The controlled growth of metal phthalocyanine thin films produces ordered molecular layers on silicon [2, 3], an ideal template for producing regular arrays of metal centres with great geometrical flexibility. The molecular film is subsequently degraded using exposure to a UV excimer light (wavelength = 172 nm) in a controlled atmosphere [4]. We have demonstrated that the UV photons rupture the intermolecular bonds, thus destroying the molecules and freeing the central metal ion which can then diffuse into the substrate. Spectroscopic techniques show that the molecular ring has been destroyed by exposure to the UV light in a repeatable and progressive way. XANES studies performed at the ESRF (ID26) demonstrate the presence of Mn in silicon without clustering and in agreement with spectra obtained from ion-implanted Mn in Si systems [5]. Our secondary ion mass spectroscopy (SIMS) studies also confirm the introduction of Mn using our technique and have allowed us to estimate the concentration of Mn to be up to $\sim 10^{20}$ atoms/cm3. Two SIMS depth profiles from the same location but taken at different times show a decrease in Mn that is approximately consistent with that expected for interstitial dopants, although it is difficult to gauge whether this is an effect of the profiling beam driving the metal atoms into the substrate or a true diffusion process. We are now keen to determine the nature of any diffusion by means of the high resolution grazing-emission x-ray fluorescence (GEXRF) method; this is non-destructive and will allow us to study the dopant depth profile with a resolution of up to 10nm as a function of time. Comparison of the measured distribution of the Mn profile with known models will allow us to identify whether the manganese forms a silicide or is present as a substitutional or interstitial dopant. In GEXRF, the depth-profiling is achieved by measuring the dependence of the x-ray fluorescence intensity on the grazing emission angle around the critical angle for x-ray radiation [6]. This dependence is uniquely related to the studied concentration depth-profile [7]. Moreover, the grazing emission geometry results in a relative enhancement of the characteristic fluorescence emission from the near-surface with respect to the substantially suppressed Si Kα fluorescence of bulk silicon.

The samples were prepared at UCL, then stored and shipped to the ESRF at low temperature. These consist of a metal phthalocyanine thin film on passivated silicon, and a series of samples that have been fully degraded by the UV lamp and chemically cleaned to remove any manganese-rich by-products formed by the processing method. No further treatment was performed on these samples at the ESRF. In addition, three samples of ion implanted Mn in Si were used as depth calibration references. The high-resolution GEXRF measurements of the concentration depth-profiles of Mn diffused in Si were performed using the von Hamos Bragg-type bent crystal spectrometer [8] of Fribourg. The latter was installed at the beam line ID21. X-ray beam energies around 6600 eV was used. To fulfill the grazing-emission condition the target was tilted close to the direction of observation defined by the Bragg angle. For such geometry the photon beam spot on the target is viewed by the crystal as a very narrow line, allowing a slit-less operation, which results in an increased detection sensitivity. The Mn Kα x-rays were diffracted by a Ge (220) crystal and recorded by a Charge Coupled Device (CCD). With this crystal, for a fixed position of the CCD, the spectrometer can cover an energy band width of 100 eV with an instrumental resolution of about 2 eV. We have previously determined that the detection limit of this technique for a Mn layer on Si is $\sim 10^{12}$ atoms/cm2; complete decomposition of the 5nm MnPc film lead to a Mn surface density of $\sim 8 \times 10^{14}$ atoms/cm2. For each target, the Mn Kα x-ray scans were acquired for exit angles between 0 and 1.0 deg. with a step of 0.01-0.05 deg. The calibration of the depth-sensitivity of the GEXRF method was obtained by measuring the x-rays from the Mn-implanted samples of known depth-profiles.

The depth resolution of the high-resolution GEXRF method provided us with a Mn distribution profile that can be next compared with that of theoretical models for substitutional, interstitial and silicide formation (for example a Gaussian profile is expected for interstitial Mn whilst a silicide would be constrained to the surface). In addition, the mapping of the Mn distribution as a function of time was performed; this will provide information about the degree of recombination enhanced diffusion that we anticipate occurs during UV irradiation and aid our development of a system in which metal dopants can be positioned in a Si lattice. It is essential that the distribution of the dopants should be assessed by GEXRF since the synthesis of well controlled atomic inclusions into Si is important for a very wide range of potential applications.

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