МАТЕРІАЛИ ДЛЯ СЕНСОРІВ

SENSOR MATERIALS

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SILICON BASED MATERIALS FOR APPLICATION IN SPINTRONICS

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Abstract

SILICON BASED MATERIALS FOR APPLICATION IN SPINTRONICS

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The effect of enhanced hydrostatic pressure (HP, up to 1.1 GPa) applied at up to 1270 K (HT) on Si:V, Si:Cr, Si:V,Cr and Si:Mn prepared by implantation of respective metallic ions (doses $1x10^{15}$ — $1x10^{16}$ cm^{-2}, at energy 160 keV or 200 keV) into (001) oriented Czochralski grown Si, has been investigated by Secondary Ion Mass Spectrometry, magnetometry and X-Ray methods.

Implantation produces amorphous silicon (a-Si) near the implanted ions range. Quasi — epitaxial re — growth of a-Si takes place at HT. The V, Cr and Mn concentration profiles do not depend markedly on HP if applied below 1000 K. Marked diffusion of implanted atoms toward the sample surface is observed in the case of processing at > 1000 K under 10^5 Pa, especially in the case of Si:Cr and Si:Mn. Under HP this diffusion is even more pronounced, re-crystallization of a-Si is retarded and the a-Si / Si interface becomes enriched with metallic atoms.

Processing of Si:V, Si:Cr and Si:Mn at ≤ 723 K results in distinct ferromagnetic ordering, detectable also above 50 K. This means that the new Si-V, Si-Cr and Si-Mn materials belonging to the family of Diluted Magnetic Semiconductors may be produced.

Keywords: silicon, implantation, vanadium, chromium, manganese, pressure, annealing, spintronics.

Анотація

МАТЕРІАЛИ, ЩО БАЗУЮТЬСЯ НА КРЕМНІЇ, ДЛЯ ЗАСТОСУВАННЯ У СПІНТРОНІЦІ

А. Місюк, Л.Чов, А. Барч, Й. Бак-Місюк, В. Осінній, М. Прущик

Методом мас-спектрометрії вторинного іона, магнітометрією і рентгеноскопічним методом було досліджено вплив підвищеного гідростатичного тиску (ГТ, до 1.1 ГПа) прикладеного до Si:V, Si:Cr, Si:V,Cr і Si:Mn при температурі аж до 1270 K, виготовлених імплантацією відповідних металевих іонів (дози 1x10[15] — 1x10[16] см[2], з енергією 160 кеВ або 200 кеВ) у (001) орієнтований Si, який вирощено методом Чохральского.

Імплантація створює аморфний кремній (a-Si) в області включеного іона. Відбувається квазі-епітаксиальний повторний ріст a-Si при високій температурі. Профілі концентрації V, Cr і Mn не залежать помітно від ГТ при температурах нижчих 1000 K. Помітна дифузія включених атомів до поверхні зразка спостерігається у випадку обробки при температурах > 1000 K при 10^5 Па, особливо у випадку Si:Cr і Si:Mn. При ГТ ця дифузія навіть більш явно виражена, перекристалізація a-Si сповільнюється і границя a-Si / Si стає збагаченою атомами металу.

Обробка Si:V, Si:Cr і Si:Mn при температурах ≤ 723 K призводить до помітного упорядкування ферромагнетика, що спостерігається також при температурах вищих 50 K. Це означає, що можуть бути отримані нові матеріали Si-V, Si- Cr і Si-Mn, які належать до класу розведених магнітних напівпровідників.

Ключові слова: кремній, імплантація, ванадій, хром, марганець, тиск, відпал, спінтроніка.

Аннотация

ОСНОВАННЫЕ НА КРЕМНИИ МАТЕРИАЛЫ ДЛЯ ПРИМЕНЕНИЯ В СПИНТРОНИКЕ

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Методом масс-спектрометрии вторичного иона, магнитометрией и рентгеноскопическим методом было исследовано влияние повышенного гидростатического давления (ГД, до 1.1 ГПа) приложенного при температуре вплоть до 1270 K к Si:V, Si:Cr, Si:V,Cr и Si:Mn, изготовленных имплантацией соответствующих металлических ионов (дозы 1x10[15] — 1x10[16] см [2], с энергией 160 кэВ или 200 кэВ) в (001) ориентированный Si, выращенный методом Чохральского.

Имплантация создает аморфный кремний (a-Si) в области внедренного иона. Происходит квази-эпитаксиальный повторный рост a-Si при высокой температуре. Профили концентрации V, Cr и Mn не зависят заметно от ГД при температурах ниже 1000 K. Заметная диффузия внедренных атомов к поверхности образца наблюдается в случае обработки при температурах > 1000 K при 10^5 Па, особенно в случае Si:Cr и Si:Mn. При ГД эта диффузия даже более явно выражена, перекристаллизация a-Si замедляется и граница a-Si / Si становится обогащенной атомами металла.

Обработка Si:V, Si:Cr и Si:Mn при температурах ≤ 723 K приводят к явному упорядочению ферромагнетика, наблюдаемому также при температурах выше 50 K. Это означает, что могут быть получены новые материалы Si-V, Si- Cr и Si-Mn, принадлежащие к классу разбавленных магнитных полупроводников.

Ключевые слова: кремний, имплантация, ванадий, хром, марганец, давление, отжиг, спинтроника.

Introduction

In recent years, the study of spintronic materials has been an active research area because of their potential use for spintronic devices to implement quantum computation [1]. Most investigations in this field are focused on ferromagnetic semiconductor, $Ga_{1-x}Mn_xAs$, and related materials [2]. Also other semiconductors / insulators such as Mn — and Cu — doped ZnO, have been reported to exhibit magnetic ordering up to room temperature [3, 4].

Ion implantation has been introduced to fabricate magnetic semiconductors such as GaN:Mn, AlGaN:Mn, AlGaN:Cr, AlGaN:Co. Recently, also silicon implanted with Mn ions, Si:Mn, has been demonstrated to posses ferromagnetic ordering up to above room temperature [5, 6].

It is apparent that Si — based spintronic semiconductors would have considerable advantage because Si — based integrated circuits (IC's) are massively produced so respective technology is well established in microelectronics.

The Si:Mn structures, prepared by implantation of silicon with Mn^+, showed especially promising structural and magnetic properties [5] after annealing at high temperature under atmospheric pressure (10^5 Pa). Also processing of Si:Mn under enhanced hydrostatic pressure (HP) at high temperatures (HT) resulted in distinct magnetic hysteresis reported at cryogenic temperatures [7, 8]. Recently magnetic ordering at low temperatures has been stated also for single crystalline Czochralski grown silicon (Cz-Si) implanted with other elements of the periodic table, preceding Mn, vanadium and chromium (Si:V and Si:Cr), especially if processed under the HT — HP conditions [9]. This means that also Si:V and Si:Cr can be considered as dilute ferromagnetic materials of possible applicability in spintronics.

Our report contributes to the understanding of the compositional, structural and magnetic properties of single crystalline silicon implanted with medium dosage of vanadium, chromium and manganese ions and processed at HT — HP.

We hope it will assist in solving of still existing controversies concerning the mechanisms of ferromagnetism in ion implanted Si — based materials, the creation of specific crystalline magnetically ordered phases [10] and quasi — ferromagnetism [11].

Experimental

To prepare Si:V, Si:Cr, co — implanted Si:V,Cr and Si:Mn, the $^{51}V^+$, $^{52}Cr^+$ or $^{55}Mn^+$ ions were implanted at room temperature into p-type (001) oriented single crystalline Cz-Si substrate with interstitial oxygen content, $c_o \approx 9x10^{17}$ cm^{-3} (Table 1).

Table 1
Characteristics of investigated samples: implantation energy (E), dose (D) and projected range of implanted ions (R_p).

Sample	E [keV]	D x 10^{15} [cm^{-2}]	R_p [nm]
Si:V	200	1	168
Si:Cr	200	1	172
Si:V,Cr	200	1 + 1	168 + 172
Si:Mn	160	10	140

The implanted samples were then processed in inert Ar atmosphere for up to 5 hr at HT ≤ 1270 K under either 10^5 Pa or HP ≤ 1.1 GPa.

The depth profiles of implanted V, Cr and Mn atoms in Si were studied by Secondary Ion Mass Spectrometry (SIMS, Cameca 5F).

The structure of Si:V, Si:Cr and Si:Mn was investigated by X-ray reciprocal space mapping (XRRSM) using a MRD-PHILIPS diffractometer. The magnetic properties at cryogenic temperatures were investigated by a SQUID magnetometer.

Results and discussion

As follows also from our earlier work [9], the sharp minimum in the V concentration at ~ 0.20 µm below the surface is observed for Si:V processed at 870 — 1270 K. The V distribution in the top 0.30 µm remains rather insensitive with respect to the processing temperatures and pressures within this temperature range (compare [9]). Similar behavior of V is observed in the Si:V,Cr samples while diffusivity of vanadium decreases slightly with HP (Fig. 1).

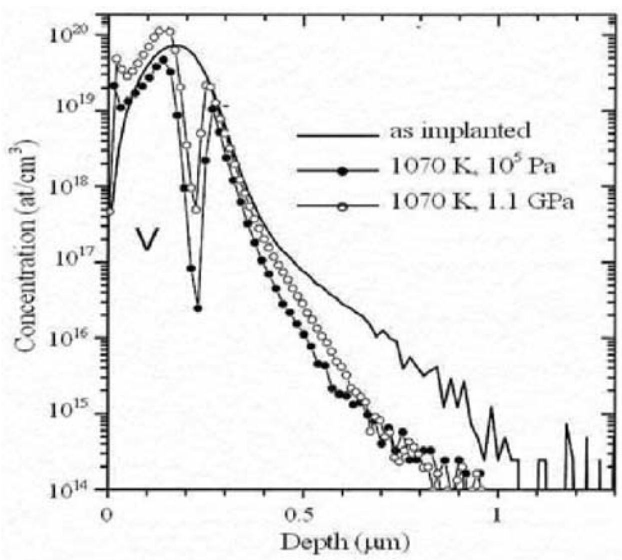

Fig. 1. SIMS depth profiles of ^{51}V in Si:V,Cr samples, as implanted and processed for 5 hr at 1070 K under 10^5 Pa and 1.1 GPa.

At E = 200 keV and D = (1 — 2) x 10^{15} cm^{-2} , the total energy introduced during implantation into silicon is above the amorphization threshold energy density for the implanted transition metal [12]. Therefore an amorphous (a-Si) layer is formed near the surface of single crystalline silicon (c-Si) up to a depth of about 0.25 µm.

At annealing, the a-Si layer is subjected to the solid phase epitaxial re -growth (SPER). This results in the movement of the a-c interface toward the Si surface. Since the solubility of V in crystalline Si is very low [13], the V ions are expelled from the re — growth region at re — crystallization, as the a-c interface moves toward the surface. Through this "snow-plow" process, a minimum in the V concentration profile was formed around ~ 0.2 μm below the surface.

The excess V ions are accumulated at the a-c interface, and eventually the V concentration reach to a point, that this process no longer can push out the excess V impurity. At temperatures in the 870 —1270 K range, the a-Si layer is converted into quasi — crystalline (polycrystalline) state and the VSi_2 silicide is formed [13].

The enthalpy of VSi_2 formation equals to 3.2 eV [13] (compare [14]), so once formed VSi_2 remains to be stable. The similarity of the V distribution within the near — surface 0.30 μm thick layer (Fig. 1) gives strong evidence that vanadium atoms formed vanadium silicides [13]. However, at a depth exceeding 0.4 μm, the tail end of the V distribution becomes distinctly narrower. One can suppose that the concentration of V in this region is low enough so that V predominately exists in the form of individual atoms. The VSi_2 nano — clusters formed around the 0.30 μm depth, trap these excess V atoms and so attract vanadium from 0.40 to 1.0 μm depth after processing at 1070 — 1270 K [9].

In the case of Si:V, the HP treatment at 870 K does not affect markedly its microstructure, implying the presence of a layered structure composed of a-Si film on the nearly perfect Si substrate.

This is in contrast with similarly treated Si:Cr. The treatment under HP results in enhanced X-ray diffuse scattering intensity from Si:Cr evidencing the presence of crystallographic defects within c-Si formed in effect of partial SPER of a-Si [9]. Possibly this is related to a little higher diffusivity of Cr in Si (~ 10^{-7} cm^2 s^{-1} and 2.1x10^{-6} cm^2 s^{-1}, respectively, for V and Cr at 1270 K [15]).

As it follows from XRRSMs, processing of both Si:V and Si:Cr at 1070 — 1270 K results in SPER of the a-Si layer. No marked structural differences between the re — growth region at < 0.30 μm and the single crystalline silicon substrate at the > 0.30 μm depth were detected after processing at 1270 K.

To contrast, the diffusion behavior of V in Si:V or Si:V,Cr, SIMS measurements of Si:Cr, implanted with Cr^+ at D = 1x10^{15} cm^{-2}, indicate that the a-c interface movement during processing is distinctly affected by HP (compare [9]).

In the case of Si:Mn processed at 1070 — 1270 K, the effect of HP on diffusivity of Mn atoms is even more pronounced: Mn atoms diffuse faster under HP, especially at 1070 K (Fig. 2, see also [7]). It seems that, in the case of prolonged (5 hr) annealing under 10^5 Pa and contrary to earlier observation for the shorter time processed Si:Mn samples [7, 15], part of Mn atoms at the > 0.25 μm depth remains at the same position as these in the as implanted sample (Fig. 2]. Possibly this is related to comparatively high solubility of Mn in Si (3x10^{16} cm^{-3} and 3x10^{14} cm^{-3}, respectively, for Mn and Cr at 1270 K [15]) and Mn gettering on some implantation — induced defects at the depth exceeding R_p.

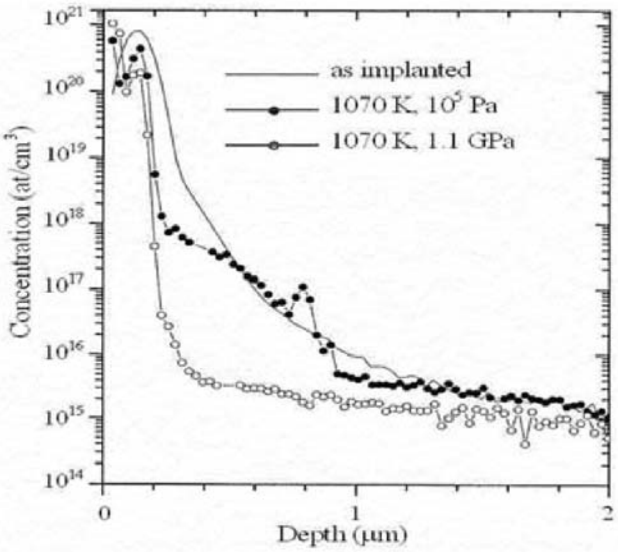

Fig. 2. SIMS depth profiles of ^{55}Mn in Si:Mn samples, as implanted and processed for 5 hr at 1070 K under 10^5 Pa and 1.1 GPa.

Processing of Si:V, Si:Cr and Si:Mn samples at ≤ 723 K can result in detectable ferromagnetic ordering (see also [7 — 9]). The Si:V samples processed at 723 K under 1.1 GPa indicated saturation magnetization (M_s) decreasing from 2.5x10^{-5} emu cm^{-2} to 2.0x10^{-5} emu cm^{-2} for temperature increasing from 5 K to 35 K [9].

The as implanted Si:Cr sample indicates distinct magnetization with both the saturation magnetization and coercivity only slightly dependent on temperature within the 5 — 50 K range.

When observing the below presented magnetization data of processed Si:Cr and Si:Mn (Figs 3 and 4), it is needed to account for the minute size of the ferromagnetic phase within the sample, containing thin damaged buried layer enriched with implanted atoms.

In a typical SQUID measurement, in addition to the desired ferromagnetic signals, the diamagnetic contribution from the Si substrate and some other paramagnetic signals are also present.

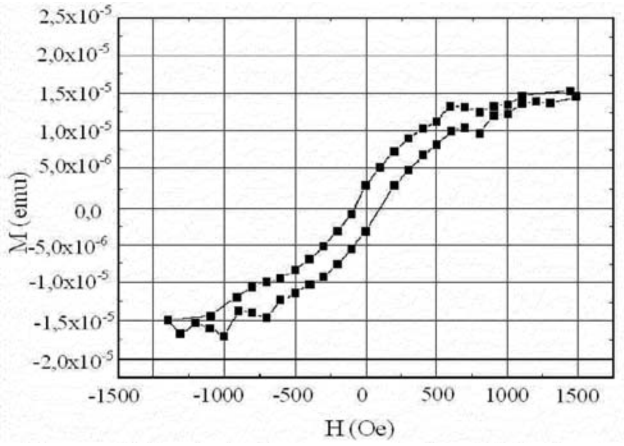

Fig. 3. Magnetization (M) versus magnetic field (H) for Si:Cr processed for 1 hr at 610 K under 1 GPa, measured at 63 K.

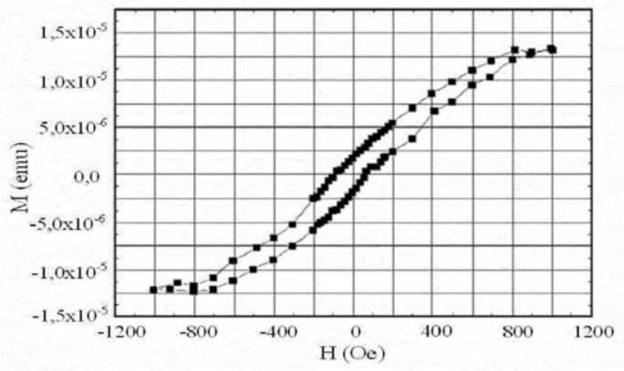

Fig. 4. Magnetization (M) versus magnetic field (H) for Si:Mn processed for 4.5 hr at 550 K under 1.05 GPa, measured at 10 K.

Recently it has been shown that also as implanted Si:Si and Si:Ar samples show ferromagnetic hysteresis loops. This property has been called "quasi — ferromagnetism" [11].

It has been suggested that certain defects created during implantation are responsible for this magnetic behavior. Specific local ordering near the implanted Mn atoms in Si:Mn can be critical also in respect of magnetic ordering [16]. In our case, observed magnetic ordering of the as implanted as well as of processed Si:V, Si:Cr and Si:Mn samples can be related in part to the mentioned quasi — ferromagnetism, moreover that observed hysteresis loops are of similar shape (compare Figs 3 and 4).

Processing of Si:V, Si:Cr and Si:Mn at ≤ 723 K results in distinctly detectable ferromagnetic ordering, detectable also above 50 K (Fig. 3). This means that the new Si-V, Si-Cr and Si-Mn materials belonging to the family of Diluted Magnetic Semiconductors can be produced by appropriate processing at HT — HP.

Further works are, however, needed to clarify the origin of the ferromagnetism in Si:V, Si:Cr and Si:Mn, as implanted and processed at HT — HP.

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