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Electrodeposition of Fe thin films on Si(1 1 1) surfaces in the presence of sodium saccharin

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Abstract

In this work we describe the fabrication of metallic Fe deposits onto Si(111) substrates using potentiostatic electrodeposition technique. The addition of sodium saccharin in the aqueous ammonium-sulfated solutions tends to inhibit the solid-state reaction between Fe and Si and enhance the protection against oxidation under air exposition compared to deposits without additive. Sodium saccharin shows to be a leveling, brightening, and stress reducing agent capable to alter the ferromagnetic behavior of the films at room temperature. The influence of the additive on the surface morphology, crystalline structure, microchemistry, and magnetism of deposits is discussed.

Keywords: Electrodeposition of metals on silicon; Saccharin as additive; Iron thin films

1. Introduction

Metallic thin films directly integrated on silicon are of significant importance due to their applications as Schottky barriers, ohmic contacts, and diffusion barriers in the integrated circuit industry. Notably, electrodeposition processes have been used to improve interconnects in large-scale integration metallization [1], to built Schottky diodes [2,3] as well as to integrate ferromagnetic materials with semiconductor microelectronics exploiting the spin injection from the ferromagnetic/semiconductor interface [4] for ultrahigh density data storage and spintronic devices technologies [5,6]. In spite of this, the processes involved in the early stage of the metal electrodeposition, especially on semiconductor surfaces, are not well understood. It is generally found that electrodeposition on semiconductors starts from surface defects and the growth itself follows a Volmer–Weber mode [7–10].

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Direct electroplating of ferromagnetic transition metal thin films onto silicon, in special Fe, is intrinsically complex due to the mutual chemical reactivity and local pH flutuations with hydrogen bubbles generating on the working electrodes. Recently, different groups demonstrated that plating solutions alternative to a Watts bath conventional consisting of metal sulfate/chloride with pH-controlling agent by boric acid, can be used to grow iron thin films and nanostructures onto silicon surfaces. Zarpellon et al. [11] reported that the Fe films electrodeposited on a Si(111) substrate exhibit submicron grains with slightly flat surfaces along with the presence of iron silicides. Lee et al. [12] have shown that α -Fe(110) films with nearly monosized nanostructures of spherical shapes on an n-type Si(111) substrate could be grown by pulsed electrodeposition in a non-aqueous solutions and Zhao et al. [13] reported the synthesis of near-monosized Fe oval-shaped nanorod particles and spherical nanoparticles by using electrodeposition on a hydrogen-terminated Si(100) surface from aqueous FeCl₃ solutions. Although these Fe core-shell nanostructures could be deposited uniformly with well defined shapes, a considerable amount of oxide shells was found, which consequently is detrimental for the magnetic properties of the Fe core itself.

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In order to enhance the metallic character and to explore physical properties of Fe deposits for Si-based spin electronics, we investigated the influence of sodium saccharin in the same ammonium sulfate solution of a previous work of our group [11]. Saccharin is an organic additive commonly used as leveling, brightening, and stress reducing agent in iron-group deposits [14–19]. Indeed, sodium saccharin salt is reported as more soluble than saccharin and its presence alters the corrosion resistance properties of CoFe deposits [20].

In this work, we investigated the morphology, crystalline structure, as well as magnetic and electronic properties of electrodeposited Fe films onto hydrogen-terminated n-type $Si(1 \ 1 \ 1)$ surfaces in the presence of sodium saccharin (SSac) salt in the ammonium sulfate solutions.

2. Experimental details

All the electrodeposition experiments were performed at room temperature using a stationary three-electrode cell with a commercial galvanostat/potentiostat (EG&G model 273A). The working electrodes were single-sided polished rectangular $(4 \text{ mm} \times 5 \text{ mm})$ phosphorous-doped n-type Si(111) wafers with a resistivity of 50–80 Ω cm at room temperature. Hydrogenterminated (111) Si surfaces were prepared after chemical removal of the native silica layer in 10% HF solution. The HF-etching is known to lead to hydrogen-terminated Si(111) surfaces which are almost atomically flat and rather stable to oxygen exposure at room temperature [21]. Gallium-aluminum alloying was used on the rear of the HF-etched Si wafers to form ohmic contacts with electrical resistance of $12 \text{ k}\Omega$ from back-tofront side. A standard saturated Ag/AgCl electrode was used as the reference electrode, being all potentials of this work given with respect to this reference electrode. A platinum disk was used as the counter electrode. Potentiostatic depositions were performed at cathodic potential of -1200 mV during 10 min from solutions of 10 mmol/L Fe(NH₄)₂(SO₄)₂, denoted as neat solution hereafter, and solutions with SSac concentrations of 0.5, 0.8, 1.0, 1.2, and 1.5 g/L (from 2.1 to 6.2 mmol/L). The deposits with SSac salt are adherent with dimmed metallic shine after 10 min. The uniformity of deposits strongly depends on both the ohmic contact on the rear Si wafers and the illumination of the Si electrolyte junction. All the electrochemical experiments were performed in bi-distilled water solutions with pH values fixed at 2.5 by addition of appropriate amounts of sulfuric acid. The electrochemical experiments were performed in a dark chamber under illumination of the electrolyte/Si interface through solution using a dichroic 12 V-50 W halogen lamp, providing a fairly uniform beam of visible light with emission spectrum mainly distributed between 400 and 700 nm. Photoelectrons in Si (energy band gap = 1.1 eV) can be generated at wavelengths below 1100 nm.

The surface morphology of the deposits was analysed by ex situ atomic force microscopy (AFM), with a scanning probe microscope (Shimadzu SPM-9500J8) working in contact mode in air at room temperature. The X-ray diffraction (XRD) measurements were performed in the conventional Bragg–Brentano geometry using Cu K α radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a commercial VG ESCA3000 system with a base pressure of 3×10^{-8} Pa, while XPS profiles were obtained by sputtering with Ar⁺ ions (2 keV, 3 μ A). A previous calibration of the sputtering rate for pure iron films gives approximately 10 nm/h. The spectra were collected using unmonochromated Mg (1253.6 eV) X-ray source and a hemispherical energy analyzer with an overall resolution of 0.8 eV at emission angle of 45°. The binding energy scale was calibrated to that of the Si 2p_{3/2} photopeak of bulk Si (99.3 eV) to avoid energy position shifts due to charging effects. Magnetization versus magnetic field curves (hysteresis loops) were performed at room temperature using an alternating gradient force magnetometer (AGFM) by applying magnetic fields parallel to the film surface at a scanning field rate of 90 Oe/s and taking points at each 300 ms.

3. Experimental results

3.1. Electrochemical analyses

Fig. 1(a) shows a set of cyclic voltammograms obtained at a sweep potential rate of 10 mV/s from the solution containing 10 mmol/L Fe(NH₄)₂(SO₄)₂ (named neat solution) and two



Fig. 1. (a) Cyclic voltammograms obtained from the solution of 10 mmol/L Fe(NH₄)₂(SO₄)₂ without SSac as well as containing 0.5 g/L SSac and 1.5 g/L SSac are shown. The voltammograms were arbitrarily shifted in the vertical scale for the sake of clarity. (b) Detail of the onset of nucleation interval in the cathodic potential scans.



Fig. 2. Potentiostatic current transients during Fe depositions at potential of -1200 mV from solutions containing different SSac amounts.

other ones with SSac concentrations of 0.5 and 1.5 g/L. For the neat solution, the potential sweep in the cathodic direction reveals a progressive reduction with a broad peak centered around $-1650 \,\mathrm{mV}$. Superimposed to the reduction wave there is a hydrogen evolution contribution with visible bubbling at the surface of the working electrode. When the potential is scanned in the positive direction, nucleation occurs accompanied by a progressive hydrogen evolution. At the end of the cyclic voltammogram, i.e., in the potential region of -900 to 0 mV, an anodic current interval is observed. As previously described, this anodic region can be assigned with oxidation of Fe to Fe^{2+} and Fe^{2+} to Fe^{3+} (or Fe to Fe^{3+} in some part) [11,13]. The addition of SSac increases the anodic current values when potential is scanned towards 0 V. The reduction wave as well as cathodic and anodic current peaks become larger and intense with addition of SSac. Notably, the voltammograms for potential scans in the cathodic direction are shifted towards more negative potentials. Consequently, the onset of nucleation potentials are also shifted towards more negative potentials with respect to the voltammogram of the neat solution, as shown in Fig. 1(b).

The nucleation and growth processes were investigated by the evolution of potentiostatic current transients. Fig. 2 shows some representative potentiostatic current transients. For solution with SSac concentration of 0.5 g/L, a cathodic current density minimum about 14 s after switching on the potential of -1200 mV is observed. It is followed by a rapid increase of the cathodic current density and a subsequent stationary regime reached after 400 s. By increasing the SSac concentration to 1.0 g/L, the cathodic current density increases more slowly and a lower stationary current density is observed. For SSac concentration of 1.5 g/L, the cathodic current density exhibits a rapid increase, reaching a maximum after $\sim 100 \text{ s}$, and subsequently it remains stationary after 250 s. We can state that the addition of SSac tends to increase the initial growth rate by change in kinetic factors It is probably associated with SSac adsorption in the H-terminated Si/electrolyte interface as well as on freshly nucleated Fe, promoting variations in the ion discharging ability along the substrate surface and affecting the hydrogen evolution, grain size of deposits (in general, the higher current density tend to have more grain boundaries and defects) and their crystalline orientation as will be shown below.

3.2. Morphology of deposits

The surface morphology of the deposits was studied by AFM. SSac addition changes significantly the morphology of the Fe deposits, as shown in Fig. 3. Even by visual observation, we can notice that the addition of SSac produced brighter samples than Fe deposits prepared without SSac. Deposits obtained in the presence of SSac exhibit a surface morphology consisting of micrometer grains having smooth surfaces, similarly to Fe deposits without SSac which are mat with root mean square (RMS) roughness of ~70 nm and sub-micrometer average granule size of $\sim 0.25 \,\mu m$ [11]. The RMS roughness and average granule sizes obtained from AFM analyses for deposits in the presence of SSac are summarized in Table 1. Addition of SSac tends to promote a leveling and brightening of deposits with a more compact juxtaposition of the grains. An exception of this general trend is found for sample obtained from solution containing 1.0 g/L SSac. This higher roughness value is perhaps a fluctuation since the RMS roughness values were averaged over sampling areas as large as 10 μ m × 10 μ m in the set of samples.

3.3. Crystalline structure

XRD analyses were performed to determine the crystalline structure and phase formation in the Fe deposits grown at potential of -1200 mV. XRD patterns (θ -2 θ scans) obtained for all deposits in the presence of SSac are shown in Fig. 4(a). All XRD patterns were normalized with respect to the intensity of the Si(111) Bragg reflection positioned at $2\theta = 28.3^{\circ}$ (not shown), which was used to orient the samples maximizing the diffracted intensity in the experiments. Fig. 4 shows the diffractograms vertically shifted in a logarithmic scale for the sake of clarity. Besides the remanescent forbidden (222) Si Bragg

Table 1

Structural and surface morphology data of the deposits obtained from the solutions containing different SSac concentrations

SSac concentration (g/L)	RMS roughness (nm)	Granule size (µm)	Strain $\Delta d/d$ (%)
0.5	_	0.6	+2.20
0.8	44	0.9	+2.18
1.0	110	1.3	+2.17
1.2	56	1.0	+2.17
1.5	54	1.1	+2.10

Root mean square roughness and average grain size were determined with dedicate software by probing sampling areas of $10 \,\mu\text{m} \times 10 \,\mu\text{m}$ for deposits in the presence of different SSac concentrations. Strain values ($\Delta d/d$) were calculated from the angular shift of Fe(1 1 0) Bragg reflection peak with respect to bulk Fe.



Fig. 3. AFM images of Fe deposits grown on Si(1 1 1) surfaces at -1200 mV after a time deposition of 10 min from solutions containing: (a) 1.5 g/L SSac; (b) 1.0 g/L SSac; (c) 0.5 g/L SSac.

reflection at $2\theta = 58.9^{\circ}$ and a small peak at $2\theta = 83.1^{\circ}$ from the Si(3 3 3), only (1 1 0), (2 0 0), and (2 1 1) Bragg reflections of body-centered cubic (bcc) iron (α -Fe) are observed when SSac concentration >0.8 g/L is present in the solutions. XRD pattern for deposit corresponding to addition of 0.5 g/L SSac is still observed a weak and broad reflection peak at $2\theta = 38.3^{\circ}$ associated with Fe silicide. These results differ from our previous work, showing that SSac is essential to inhibit the formation of Fe silicides underlayers and oxy-hydroxides [11]. The increase in SSac amount improves the preferential (1 1 0)-texture of Fe deposits, as shown in Fig. 4(b). As can be seen, the increase of SSac in the solutions has an exponential influence on the area



Fig. 4. (a) X-ray diffraction patterns of Fe deposits in the presence of SSac salt. SSac amounts and identification of Bragg reflections are indicating alongside diffractograms which are vertically shifted in a logarithmic scale for the sake of clarity. (b) Area ratio of Bragg reflection peaks (200) and (211) with respect to (110) indicating the texture in the polycrystalline deposits. The asterisk (*) indicates a peak from the Cu K β radiation.

of (1 1 0) peak with respect to (2 0 0) and (2 1 1) ones. We evaluate the strain in the deposits by taking into account the angular shift of the Fe(1 1 0) Bragg reflection peaks with respect to bulk Fe value (namely $\Delta d/d$). The strain values (~2%) displayed in Table 1 were calculated from the angular shift (typically is found $\Delta(2\theta) \sim 0.9^{\circ}$ for angular steps of ~0.03° in the XRD patterns) of the centroid of the peaks corresponding to the Fe(1 1 0) reflection shown in Fig. 4. The addition of SSac tends to reduce the strain, promoting a stress relaxation in the expanded Fe lattice. Thus, the influence of SSac is similar to that of saccharin which is an effective internal stress reducer [14,22–24].

3.4. X-ray photoemission spectroscopy

XPS analyses indicate that all deposits exhibit an elemental composition consisting of Fe, Si, and O with a superficial residual layer with N and C adsorbates. XPS analyses for all deposits obtained at potential of -1200 mV do not show the presence of neither sulfur nor sodium i.e., SSac incorporation in the deposits is not observed. The S incorporation was detected only for deposits obtained from the solutions containing 1.5 g/L SSac under a potential of -1500 mV. Besides, the incorporation of S in these deposits occured without trace of Na, strongly indicating the dissociation of the SSac and their complexation, as already reported by several groups [25–28]. We address here the



Fig. 5. Fe 2p core-level spectra for Fe deposits obtained from the solutions containing (a) 0.5 g/L and (b) 1.5 g/L SSac. XPS spectra of as-deposited samples and after cummulative exposure to argon ion bombardment for several etching times are shown. Spectral components associated with superficial oxide and metallic Fe are indicated.

deposits obtained at the potential of -1200 mV in which sulfur incorporation is not observed. The small silicon photoemission signal is observed for all the deposits obtained in the presence of SSac. It is indicating that a three-dimensional islands effectively occurs onto Si substrate which confirm the Volmer–Weber growth mode. Fig. 5(a) and (b) shows the Fe 2p core-level spectra for Fe deposits grown in the presence of 0.5 and 1.5 g/L SSac, respectively. XPS spectra collected from as-deposited samples and after argon ion bombardment for several etching times are shown. The sputter-etching progressively reveals a metallic Fe component underneath a superficial oxygen-rich layer, consisting of Fe oxide.

3.5. Magnetic behavior

Fig. 6 shows a set of normalized hysteresis loops measured at room temperature with magnetic fields applied in the film plane for deposits obtained from the solutions containing different SSac concentrations. The magnetization is normalized with respect to saturation magnetization M_s at maximum applied field. A clear ferromagnetic behavior with moderate remanence ratio (36–41% M_s) is observed for deposits with different SSac concentrations. The addition of sodium saccharin is also accompanied by a significant reduction in the coercive field with respect



Fig. 6. Hysteresis cycles measured at room temperature for deposits obtained from solutions containing different SSac concentrations. The magnetic field was applied in the film plane which behaves as an isotropic magnetic plane and the magnetization is normalized to the saturation magnetization.

to pure iron films which are covered by Fe oxides. Since the presence of Fe oxides are superficial compared to total thickness of samples, the significant lowering of coercive field values with addition of SSac in the solutions is probably due to different crystalline structures and the size and separation of the grains. Both coercive field and remanence ratio values are given in Table 2. All deposits exhibit easy magnetic plane in the film plane with equivalent remanence ratio with respect to saturation magnetization. Deposits obtained from solutions without SSac exhibited a small hysteretic loop at low fields superimposed to a predominant linear paramagnetic response at room temperature, indicating the detrimental influence of silicides as well as oxy-hydroxide formations for ferromagnetism [11].

4. Discussion

The mechanism of saccharin action during iron and iron alloys deposition has been discussed many times in the literature [14–19]. The saccharin is pointed out as one of the most effective internal stress reducer, caused by inclusion of sulfur in the deposit by the intermediary sulfonamide group, and often helps to decrease or eliminate hazes of the deposits [14–24]. The sulfur incorporation may be realized by electrostatic interaction with a negative charged electrode or by chemisorption. Shifts of nucleation potentials towards more negative potentials are expected due to the decrease of the deposition rate through a surface blocking and solution chelating process [14].

Table 2

Coercive field and remanence ratio (relative to saturation magnetization M_s) values obtained from hysteresis loops for deposits obtained from the solutions containing different SSac concentrations

SSac concentration (g/L)	Coercive field (Oe)	Remanence (% M_s)
0.5	429	41
1.0	397	36
1.5	336	39

The molecular structure of the SSac is similar to saccharin with sodium atoms replacing the hydrogen bound to nitrogen. The influence of SSac in the electrodeposition of Fe deposits on Si can be expected to lead to the same behavior. Our experimental observations confirm results published in the literature, concerning the influence of saccharin on Fe-group deposits. Notably, the addition of SSac results in a fairly broad Fe reduction wave, superimposed to hydrogen evolution and nucleation potentials shifts towards more negative potentials with respect to the cycle of the solution without SSac. It is difficult, however, to ascertain what is the cause for the observed shifts in the reduction waves, since different electron transfer paths for the reduction of electroactive species at the Si/electrolyte interface could occur due to SSac affinity with the ions present in the solution and change the diffusion of cations towards the cathode because of this complexation [29]. It is also reliable that changes in the hydrogen evolution occurs due to SSac addition. It has been shown that the general chemical formula of the metal-saccharin complex has the iron ion bound to the nitrogen atom in the sulfonamide group. SSac adsorption in the H-terminated Si/electrolyte interface could promote variations in the ion discharging ability along the substrate surface altering the Schottky barrier height (SBH) formation in the n-type Si/eletrolyte interface. A SBH value of about 0.7 eV is reported for CoFe/Si interface [30], however this value cannot explain the necessary cathodic potential for the nucleation wave observed in our experiments. Since Fe silicides formation [11] is tremendously inhibited by addition of SSac and current densities exhibit drastic changes for deposition times (smaller than 100 s) corresponding to a coverage fraction of Si substrate smaller than 30-40% of total area, we cannot discard that important changes are introduced in the nucleation and growth processes by the addition of SSac and its adsorption on the hydrogen-terminated Si surface. Therefore, SSac adsorption on hydrogen-terminated Si surface and freshly nucleated Fe together with complexation mechanism in solution are closely related to the small cathodic shifts observed at the onset the cathodic current in the cyclovoltammograms presented in Fig. 1.

Many changes in growth kinetics and deposit structure are introduced by the addition of SSac in the solution indicating the influence of SSac adsorption on freshly nucleated Fe. The potentiostatic transients taken at a potential of $-1200 \,\mathrm{mV}$ exhibit an evolution in a time scale of several hundred seconds, as shown in Fig. 2. We describe the time evolution of potentiostatic transients as follows. At the beginning, a sporadic and heterogeneous nucleation occurs due to a random occupation of the preferential active sites on the initial surface. Next, the number of nuclei growing on the Si surface is rapidly saturated and, subsequently, a further reduction of Fe ionic species on the already deposited nuclei predominates; i.e., nucleation and growth are in favor of the deposition on the covered zones. The average granule sizes scattered in micrometer scale in the AFM images and Si photoemission signal observed by XPS corroborate these assumptions and is also indicating that Volmer-Weber threedimensional growth mode [14–19] occurs. The addition of SSac increases the Fe ion discharging ability, facilitating a diffusionlimited aggregation of ions in juxtaposed three-dimensional islands with a slightly flat growth front. The inhibition of silicide and oxy-hydroxide formation occurs with an enlargement of the granule sizes. As mentioned in Section 3.4, the investigation of deposition in presence of 1.5 g/L SSac under a potential of -1500 mV reveals the SSac dissociation with sulfur incorporation in deposits with evidence of local disruption of the film due to a severe hydrogen evolution. The potentiostatic transients, in this case, exhibit current densities reaching stationary values as large as 80 A/cm^2 with high noise level as a consequence of the hydrogen gas bubble evolution. Compact and smooth (RMS roughness is 21 nm) deposits are formed with small granule sizes ($0.8 \mu \text{m}$). However, the formation of Fe silicides and oxyhydroxides is observed by XRD. It is indicating that moderate cathodic potential to inhibit SSac dissociation and incorporation in the deposits are necessary to avoid silicide and oxyhydroxide formation.

Fe growth on a clean Si surface in non-equilibrium conditions (like electrochemical conditions) easily leads to unusual silicides formation as a result of stress accommodation at the interface, variations in the stoichiometry of initial deposit and islanding kinetic factors. In our previous work [11], XRD and XPS data present evidence that metastables Fe₂Si and Fe₅Si₃ are formed and their Bragg reflection peaks increase upon annealing together with a clear increase in the Fe crystalline quality attested by intensity increase of the α -Fe(011). In the present case, the XRD patterns shown in Fig. 4(a) reveal that α -Fe is formed. Although significant, only small relaxation (2.2–2.1%) of the expanded Fe lattice is observed in the presence of SSac (from 0.5 to 1.1 g/L SSac). It was found a crystalline texture with predominance of the densest atomic plane (110) of α -Fe in the film plane predominates when increasing SSac, as shown in Fig. 4(b). However, the addition of SSac while keeping the pH and temperature of the electrolyte stable have a small influence in the residual strain. It is probably connected with the higher growth rates imposed by SSac (as shown in Fig. 2). A faster nucleation is more effective to inhibit the interface reaction than induce a strain relaxation in the deposits.

A predominant metallic Fe nature of deposits even exposed to the air is confirmed by XPS. Comparing the XPS spectra evolution of Fig. 5(a) and (b) for equivalent etching times, we observe that a metallic Fe component becomes predominant for deposits obtained from solutions with a higher SSac concentration. Since the surface morphology and ion decapping can be considered the same, we may conclude that SSac tends to inhibit the oxidation of the samples exposed to the air. This assumption is also corroborated by XRD analyses since a higher (1 1 0)-texture in the deposits with 1.5 g/L SSac tends to reduce their oxidation front.

The structural changes imposed by SSac present in the solutions are apparently significant to affect the room temperature hysteresis cycle of the ferromagnetic deposits. The small strain relaxation and densest juxtaposition of grains are probably associated with reduction of the coercive fields when increasing SSac. Besides, bulk Fe has an easy and hard magnetic axis along the $\langle 1 0 0 \rangle$ and $\langle 1 1 1 \rangle$ crystalline directions, respectively. Then, the crystalline texture with (1 1 0) planes preferentially oriented parallel to the strain-relaxed film plane is reasonable to result in almost isotropic easy magnetic plane with a small remanence ratio as observed. Thus, concerning the change of the texture of deposits and their influence in the magnetization behavior, we can state that our results indicate that saturation magnetization is reached at fields smaller than 5 kOe with all deposits exhibiting ferromagnetism at room temperaure with easy magnetic plane in the film plane.

Our present results opens, therefore, the possibility to explore Si-based spin electronic devices, such as proposed spin MOSFET in which a MOS gate capacitor is combined with ferromagnetic source and drain [30].

5. Conclusions

In summary, the electrochemical conditions for the direct electrodeposition of iron thin films onto hydrogen-terminated Si(111) surfaces were determined by appropriated dilution of sodium saccharin salt in the aqueous ammonium-sulfated iron solutions. Good quality metallic Fe deposits having a bodycentered cubic structure were obtained. The film morphology, surface chemistry, structure, magnetic, and electronic properties were analysed by various techniques revealing that spontaneous reaction between Fe deposits and Si surface, observed at room temperature with formation of oxides and polycrystalline silicides, have been inhibited by using sodium saccharin. We believe that electrochemical synthesis of iron films with this additive is a practical mainstream process for the integration of the ferromagnetic films to silicon.

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