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Formation and magnetic properties of ultrathin cobalt silicides films on Si surface

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Abstract. High-resolution photoelectron spectroscopy with synchrotron radiation and magnetic linear dichroism in Co 3p core-level photoemission have been used to study the initial stages of formation and ferromagnetic ordering of Co/Si(100) and Co/Si(111) interfaces. The correlation between the phase composition, electronic structure and magnetic behavior of the interfaces has been established during Co deposition on Si surface and subsequent sample annealing. It is shown that ferromagnetic ordering has a threshold nature and arises after the deposition of 6 Å of Co in both systems. At higher Co coverages a continuous film of a Si solid solution in cobalt is found to develop. Further increase of ferromagnetic ordering of the interface is caused by the growth of pure metal film. Annealing of the samples covered with a Co film of few nm thickness leads to the gradual disappearance of the metal film and formation of four silicide phases: a metastable ferromagnetic Co_3Si silicide obtained at room temperature for the first time and three stable non-magnetic cobalt silicides: Co_2Si, CoSi and $CoSi_2$. It is shown that solid-phase reactions start at ~250 °C and ~320 °C in Co/Si(100) and Co/Si(111) systems respectively.

Keywords: cobalt, magnetic properties, silicides, photoelectron spectroscopy

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Формирование и магнитные свойства ультратонких пленок силицидов кобальта на поверхности кремния

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Аннотация. Начальные стадии формирования и ферромагнитное упорядочение интерфейсов Co/Si(100) и Co/Si(111) были исследованы с помощью фотоэлектронной спектроскопии высокого разрешения с использованием синхротронного излучения и магнитного линейного дихроизма в фотоэмиссии Co 3p остовных уровней. Показано, что ферромагнитное упорядочение носит пороговый характер и возникает после напыления 6 Å Co в обеих системах. Отжиг образцов приводит к образованию четырех

силицидных фаз: метастабильного ферромагнитного силицида Co_3Si, впервые полученного при комнатной температуре, и трех стабильных немагнитных силицидов кобальта: Co_2Si, CoSi и $CoSi_2$.

Ключевые слова: магнитные свойства, силициды, фотоэлектронная спектроскопия

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Introduction

In the past decades, formation of thin cobalt silicide films on silicon has drawn much attention because it represents interesting science and promising applications [1–3]. The initial effort was focused on the fabrication of defect-free epitaxial $CoSi_2$ films. Low resistivity, high thermal stability and small lattice mismatch with silicon allow the films to be used as very attractive contact and interconnect materials in integrated circuit technology [1, 2]. A new impetus to this research came from the studies of magnetic Si-based heterostructures and the mechanism of interlayer exchange coupling through nonmetallic spacers in Co/Si multilayers [3]. These structures are of especially high technological interest due to the possibility of being used as low-resistivity contacts in electronic devices, which could save steps in the manufacturing process. However, in contrast to Fe/Si system, Co/Si heterostructures have been much less studied and available experimental results are contradictory [3]. The reason for the different magnetic behavior is a very high sensitivity of diffusion processes at the Co/Si interface to experimental conditions, such as the initial state of the substrate surface, the metal deposition rate, and others. For example, the authors of Ref. [2] have found that Co film grows on the Si(100) surface in the layer-by-layer mode at room temperature. As to magnetic properties of Co/Si interface there are only few reports related to the Si(111) surface [4]. These studies were performed in situ using surface magneto-optic Kerr effect and scanning tunneling microscopy. However, the influence of both the chemical composition of the interfacial layers and their electronic structure on the magnetic properties of a Co/Si interface is poorly understood. In this article, the initial stages of Co/Si(100)2×1 and Co/Si(111)7×7 interfaces formation have been studied for the first time by high resolution photoelectron spectroscopy as well as their ferromagnetic ordering have been investigated using magnetic linear dichroism method. The use of these surface sensitive techniques in the frame of a single experiment allowed to reveal certain correlations between the phase composition, electronic structure, and magnetic behavior of the interfaces.

Materials and Methods

The experiments were carried out using the Russian-German beamline at the Helmholtz-Zentrum Berlin (BESSY). Most of the spectra were measured at 135 eV, the energy at which the surface sensitivity of the Si 2p spectra has a maximum [5]. The magnetic properties of the interface were analyzed by a method based on magnetic linear dichroism (MLD) in Co 3p photoemission. The energy position and shape of the photoelectron peak measured within a narrow solid angle around the normal to the sample surface appears to vary with the sample magnetization [6]. The sample to be studied was magnetized with a pair of Helmholtz coils fixed inside the vacuum chamber. The measurements of the Co 3p spectra were performed in remanence.

The pure Si(100)2×1 and Si(111)7×7 surfaces were prepared in the conventional manner by annealing the samples to 1200 °C for several seconds and then slowly cooling them to room temperature. The procedure provided a well-defined low-energy electron diffraction pattern (LEED) and a surface uncontaminated with carbon and oxygen. The chemical composition of the surfaces was monitored using the photoelectron spectra. Cobalt was evaporated from a thoroughly degassed source, in which a wire of highly purified material (99.99 %) was heated by electron

bombardment. The Co flux was 0.3 Å/min in the standard operation mode. The film thickness was varied up to 20 Å. To study thermostimulated reactions at the interface, the samples were subjected to 5 min annealing at fixed temperatures which were varied from room temperature to 600 °C. All the photoelectron spectra were measured at room temperature in vacuum less than 1.5×10^{-10} mbar.

Results and Discussion

The typical Si 2p spectra taken during the deposition of Co on Si(100)2×1 and Si(111)7×7 at room temperature are shown in Fig. 1. It is seen that the line shape is quite sensitive to the Co coverage demonstrating change of chemical state of Si atoms during the deposition of Co. More detailed information can be obtained using decomposition of the spectra into surface and bulk components by using the least-square fitting procedure. This was done as described in [7]. Each spectral component was approximated by the spin-orbit doublet with the splitting into $2p_{3/2-}$ and $2p_{1/2-}$ sublevels equal to 0.61 eV. The line intensity ratio for these sublevels with the account of their populations was taken to be two. Fig. 1 also shows the results of spectra decomposition. According to the data reported in Ref. [8], the initial spectrum of a reconstructed Si(100)2×1 surface includes a bulk mode (*B*), two modes (S_u and S_d) for the top and bottom dimer atoms, and the modes for the first (S_1') and the second (S_1'') silicon monolayers. The initial spectrum of the Si(111)7×7 surface consists of bulk mode *B* and four surface modes of S_A, S_R, S_P, and SD that can be assigned to adatoms, rest atoms, pedestal atoms, and dimers, respectively.

In both cases, the next spectra, measured after Co deposition, show no surface modes of Si atoms, indicating the absence of Si surface reconstruction or exposed sites of the substrate. Instead of the surface components, we find new features in the Si 2p spectrum: *I*, *C* and *S* modes. The *I* mode can be attributed to an ultrathin CoSi interface film, on which the phase of the C mode is to be formed. Mode *C* can be assigned to silicon atoms dissolved in the cobalt matrix. A new component *S* exhibits a negative energy shift relative to mode *C*. Such a shift is typical of surface components accompanying volume modes in the spectra of solid solutions and silicides. Thus, the *S* component is to be identified to silicon atoms segregated on the surface. For both investigated systems we obtained the same modes, but their intensities are different.

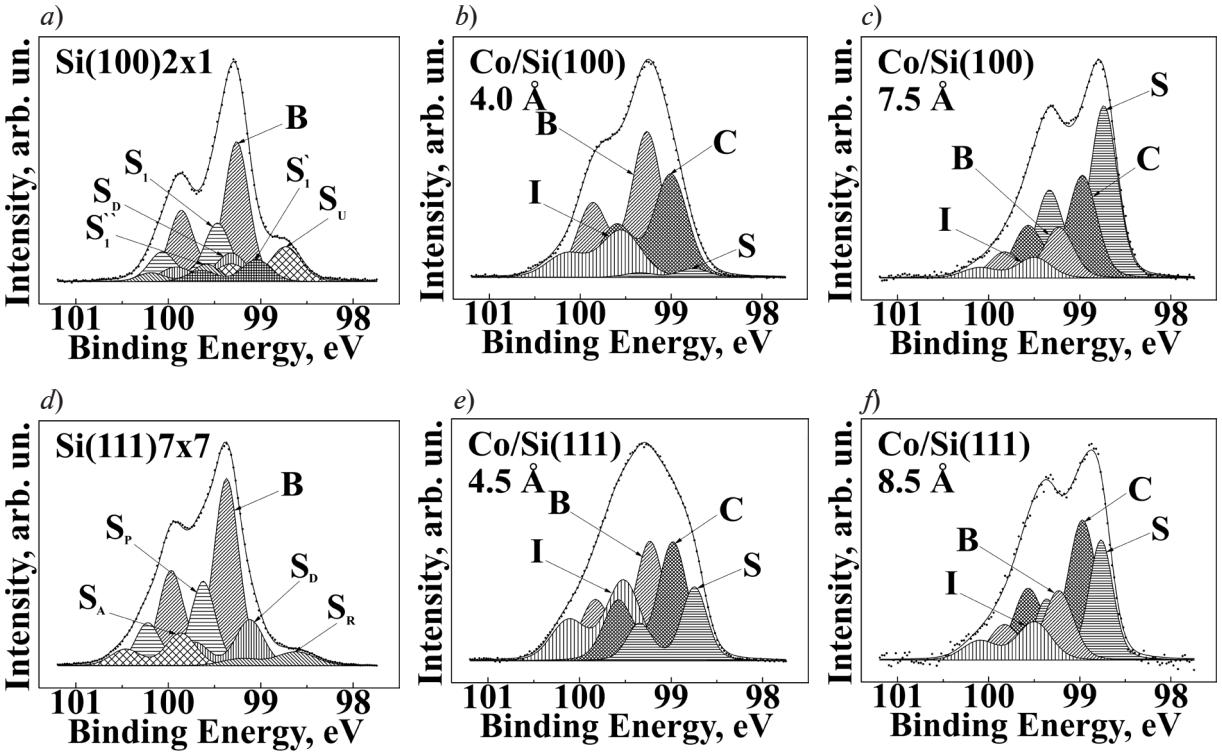

Fig. 1. Si 2p core-level spectra taken from Si(100)2×1 and Si(111)7×7 surfaces and after the deposition of Co films of different thickness at room temperature. Their decomposition is shown as well

Consider now the solid-phase reactions occurring at the interface during annealing of the samples covered with 16 Å of Co. The spectra of valence electrons obtained after the deposition of cobalt on Si(100) surface and taken after each annealing of the sample are illustrated in Fig. 2. One can see that there are the curves of three types corresponding to the different formed phases. The curves of the first type are observed at temperatures less than 340 °C. These spectra are similar to the first curve measured after Co deposition. The spectra of the second type can be seen at temperatures equal to 360 °C and 420 °C. According to Ref. [9], they correspond to the stable monosilicide ε-CoSi. Finally, the spectrum taken after the annealing at 600 °C demonstrates the characteristic features of $CoSi_2$ silicide [10].

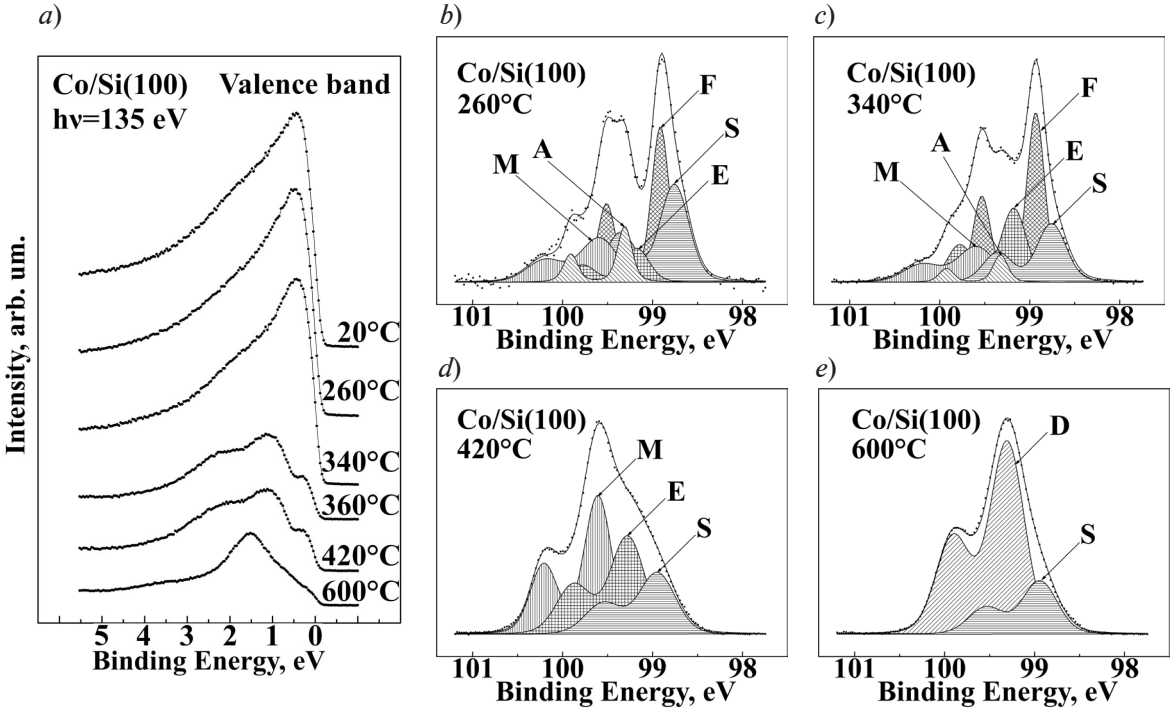

Fig. 2. Valence band and Si 2p spectra taken from the Si(100)2×1 surface with 16 Å of Co deposited at room temperature and after the sample annealing to different temperatures

The initial Si 2p spectrum measured after the deposition of 16 Å of Co shows only traces of the Si line due to its damping by the Co layer. Well defined Si 2p signal indicating a start of solid-phase reactions in the analyzed layer was found after annealing of Si(100) sample at ~ 260 °C (Fig. 2). The spectrum taken after annealing at 260 °C consists of several modes (*A*, *S*, *M*, *E*, *F*), two of them have already been obtained before the sample annealing. The first one is the anomalously narrow mode typical for silicon atoms adsorbed on the metal surface. We observed this mode after the deposition of 12 Å of Co. The second one is *S* mode of segregated Si. The new M mode corresponds to the cobalt monosilicide since this mode dominates in the Si 2p spectra after annealing at 420 °C and the corresponding valence band is typical of CoSi. The E mode corresponds to Co_2Si silicide (we obtained the value of binding energy for this mode after annealing of Si(110) sample at 360 °C in another experiment).

The interpretation of the F mode is of the greatest interest. This mode is the most pronounced in the temperature range from 260 to 340 °C. Its energy position is close to the binding energy of the silicon atoms in the solid solution Co-Si. However, the width of the line (250 meV) is significantly lower than the corresponding characteristic value of the solid solution mode (420 meV), indicating the formation of another phase. The only remaining known cobalt silicide is Co_3Si (our further calculation also showed that the concentration ratio of Co and Si is close to 3:1). However, this compound is stable only in a narrow temperature range in the area of 1200 °C. In our case, due to the non-equilibrium conditions this is a metastable phase. The further temperature rise to 340 °C slightly reduces the segregated Si and adatoms features and increases the Co_2Si mode intensity. The shape of the spectrum line completely changes after

annealing at 420 °C: Co_3Si silicide and adatoms modes disappear and the monosilicide feature greatly increases. The last solid-phase reaction in this system was observed at 600 °C. Instead of the *M* and *E* modes, we found a new *D* feature. Since the whole Si 2p spectrum consists only of this mode with a small mode of segregated Si and a valence band spectrum is typical of disilicide, we concluded that the *D* mode corresponds to $CoSi_2$ silicide. Since the process of silicide formation is due to the bonds breaking in the silicon substrate and diffusion of released silicon atoms through the interface, the temperature of silicide formation can depend on the orientation of the substrate.

Consider now the magnetic properties of Co/Si interface observed during the Co deposition. Representative Co 3p spectra taken after the deposition of increasing Co doses at room temperature for Co/Si(100) surface are present in the left side of Fig. 3. They were obtained for two oppositely directed sample magnetizations parallel to its surface and oriented, accordingly, up (M_{up}) and down (M_{down}). In order to show the possible spectral differences between the curves more clearly we plotted the appropriate difference curves. The effect was detected after the deposition of 6 Å of Co. Maxima and minima appear on the difference curves, corresponding, according to [11], to the sublevels $m_j = \pm 3/2$ of the Co 3p multiplet.

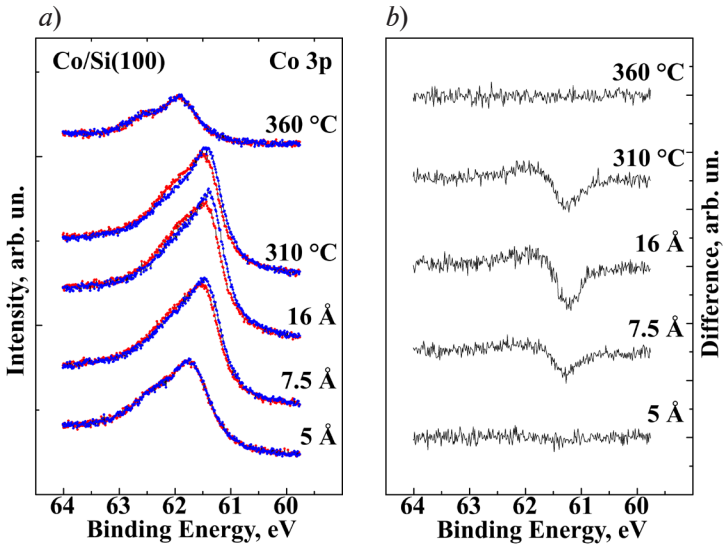

Fig. 3. Co 3p electron spectra taken after deposition of Co of different thickness at room temperature for two opposite directions of the magnetic field (*a*) and their difference curves (*b*)

The magnetic asymmetry of a difference spectrum is commonly estimated using the quantity *S* defined as follows:

$$S(E) = [I_{up}(E) - I_{down}(E)]/[I_{up}(E) + I_{down}(E)].$$

The normalization of the difference spectrum to the total intensity makes *S* dimensionless value independent of the Co content in the analyzing surface range of the sample. A quantitative parameter to describe the effect is the amplitude *A* of the magnetic asymmetry defined as:

$$A = \{\mathrm{MAX}[S(E)] - \mathrm{MIN}[S(E)]\} \times 100\%,$$

where the values of MAX[*S*(*E*)] and MIN[*S*(*E*)] correspond to the above sublevels $m_{\pm 3/2}$. The parameter A characterizes its remanent magnetization. The ferromagnetic ordering of the interface has a threshold nature and arises after the deposition of ~ 6 Å Co. This coverage corresponds to the formation of Co-Si solid solution. The absence of in-plane ferromagnetic ordering in the range of Co coverages less than 6 Å may be explained by abrupt change in the direction of magnetization of Co-Si ferromagnetic layer with an increase of its thickness or with the size dependence of the Curie temperature, which is typical for thin films [4]. The value of the amplitude A for Co/Si(100) system is significantly higher than that for Co/Si(111) one. We suppose that it may be explained by the difference in the morphology of the films.

Let us consider now the influence of the sample annealing on a surface ferromagnetic ordering. Co 3p spectra taken in these experiments were measured also for two oppositely directed magnetizations. The obtained dependencies of the A amplitude on the annealing temperature are presented in Fig. 4. As one can see in figure, the magnetic ordering of the surface remains constant up to 260 °C for Co/Si(100). Further, when the temperature rises to 310 °C, it is reduced from 17% to ~13 % and remains constant until annealing at 340 °C. Finally, it falls to zero at 360 °C. As for the Co/Si(111) system, the amplitude of magnetic asymmetry remains constant up to 320 °C, than it rapidly falls to zero as well.

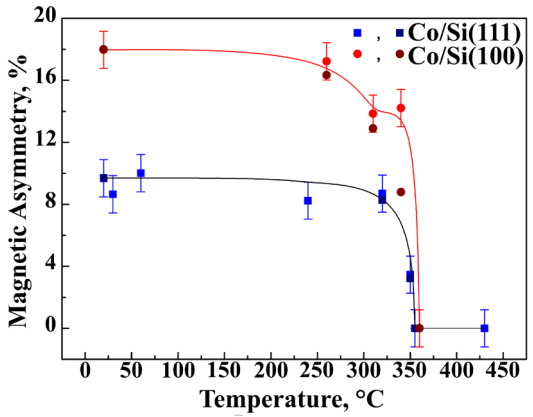

Fig. 4. Dependence of magnetic asymmetry amplitude A of the Co 3p spectra on the annealing temperature

The decline of the amplitude A with temperature raise correlates well with the decrease of metal Co film thickness on the sample surface and the formation of Co_3Si silicide in the analyzed surface layer. MLD effect remains after the disappearance of metal Co film but vanishes after the disappearance of Co_3Si silicide during the sample annealing at 360 °C.

Conclusion

In this paper, we established the correlations between the phase composition and magnetic properties of ultrathin films formed on the Si(100)2×1 and Si(111)7×7 surfaces upon Co deposition at room temperature and subsequent annealing of the samples to 600 °C. In particular, it was found that the interface silicide CoSi and Co-Si solid solution are formed at the initial stage of Co deposition on Si substrate. It was shown that in-plane ferromagnetic ordering has a threshold nature and was found to appear at Co coverage of 6 Å for both systems corresponding to solid-solution phase. After the samples annealing, the first synthesized phases are the metastable ferromagnetic Co_3Si and non-magnetic Co_2Si silicides. They transform to CoSi and $CoSi_2$ silicides at higher temperatures. The temperature ranges of stability and values of Si 2p binding energies were determined for all mentioned silicides formed on Si(100) and Si(111) surfaces.

REFERENCES

1. **Bulle-Lieuwma C.W.T.,** Epitaxial growth of $CoSi_2$/Si structures, Applied Surface Science. 1 (68) (1993) 1–18.

2. **Ilge B., Palasantzas G., De Nijs J., Geerlings L.G.,** The temperature evolution of ultra-thin films in solid-phase reaction of Co with Si (111) studied by scanning tunneling microscopy, Surface Science. 1–2 (414) (1998) 279–289.

3. **Yaacoub N., Meny Ch., Ulhaq-Bouillet C., Acosta M., Panissod P.,** Short period magnetic coupling oscillations in Co/Si multilayers: Role of crystallization and interface quality, Physical Review. 75 (2007).

4. **Chang H.W., Tsay J.S., Hung Y.C., Yuan F.T., Chan W.Y., Su W.B., Chang C.S., Yao Y.D.,** Magnetic properties and microstructure of ultrathin Co/Si (111) films, Applied Physics. 101 (2007).

5. **Hong S., Wetzel P., Gewinner G., Bolmont D., Pirri C.,** Formation of epitaxial $Fe_{3-x}Si_{1+x}$ $(0 \le x \le 1)$ silicides on Si (111), Applied Physics. 9 (78) (1995) 5404–5411.

6. **Roth Ch., Hillebrecht F.U., Rose H.B., Kisker E.,** Linear magnetic dichroism in angular resolved Fe 3p core level photoemission, Physics Review Letters. 70 (1993).

7. **Gomoyunova M.V., Pronin I.I., Malygin D.E., Gall N.R., Vyalikh D.V., Molodtsov S.L.,** Photoemission experiments and density functional calculations for the W(1 1 2) stepped surface with submonolayer Au coverages, Surface Science. 600 (2006) 2449

8. **Pi T.-W., Ouyang C.-P., Wen J.-F., Tien L.-S., Hwang J., Cheng Z.C.-P., Wertheim G.K.,** Early nucleation on the Si (100)-2×1 surface, Surface Science. 1–3 (514) (2002) 327–331.

9. **Pirri C., Hong S., Tuilier M. H., Wetzel P., Gewinner G., Cortés R.,** Epitaxy of $CoSi_x$ ($1 < x < 2$) silicides on Si (111) studied by photoemission and extended x-ray-absorption fine-structure techniques, Physical Review. 53 (1996).

10. **Gomoyunova M.V., Pronin I.I., Gall N.R., Vyalikh D.V., Molodtsov S.L.,** Interaction of cobalt with the Si (100)2×1 surface studied by photoelectron spectroscopy, Surface Science. 1–3 (578) (2005) 174–182.

11. **Sirotti F., Rossi G.,** Magnetic asymmetry in photoemission from Fe (100) with linearly polarized synchrotron radiation, Physical Review. 49 (1994).

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