Conference materials
UDC 539.216
DOI: https://doi.org/10.18721/JPM.153.122

Effect of thickness and annealing of the Si(001)2×1-Cu wetting layer on the morphology of layered nanofilms based on Fe, Co, and Cu and their ferromagnetic properties

N. I. Plyusnin[1, 2] ✉, P. A. Usachev[1], V. V. Pavlov [1]

[1] Ioffe Institute, St. Petersburg, Russia;

[2] S. M. Budyonny Communications Academy of the Ministry of Defense of the Russian Federation, St. Petersburg, Russia

✉ plusnin@dvo.ru

Abstract: Layered nanofilms based on Fe, Co, and Cu were grown on Si(001)2×1-Cu wetting layers with thicknesses of 1 and 2 ML and studied using the AES, EELS, and LEED methods in an ultrahigh vacuum chamber. After unloading into air, the samples were studied by AFM and MOKE methods. It was found that an increase in the thickness and annealing of the Si(001)2×1-Cu wetting layer increase the agglomeration of nanofilms and, as a consequence, their magnetization and coercive force. Although, annealing the Cu wetting layer reduces the degree of squareness of the magnetic hysteresis loop.

Keywords: multilayer films, wetting layer, growth, agglomeration, morphology, metals, silicon substrate, hysteresis loop, atomic force microscopy, magneto-optical Kerr effect

Citation: Plyusnin N. I., Usachev P. A., Pavlov V. V., Effect of thickness and annealing of the Si(001)2×1-Cu wetting layer on the morphology of layered nanofilms based on Fe, Co, and Cu and their ferromagnetic properties, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.1) (2022) 131–136. DOI: https://doi.org/10.18721/JPM.153.122

Материалы конференции
УДК 539.216
DOI: https://doi.org/10.18721/JPM.153.122

Влияние толщины и отжига смачивающего слоя Si(001)2×1-Cu на морфологию слоистых нанопленок на основе Fe, Co и Cu и их ферромагнитные свойства

Н.И. Плюснин [1, 2] ✉, П.А. Усачев [1], В.В. Павлов [1]

[1] Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия;

[2] Академия связи им. С.М. Буденного МО РФ, Санкт-Петербург, Россия

✉ plusnin@dvo.ru

Аннотация. Слоистые нанопленки на основе Fe, Co и Cu были выращены на смачивающих слоях Si(001)2×1-Cu с толщинами 1 ML и 2 ML и исследованы методами AES, EELS и LEED в сверхвысоковакуумной камере. После выгрузки на воздух образцы были исследованы методами AFM и MOKE. Было обнаружено, что увеличение толщины и отжиг смачивающего слоя Si(001)2×1-Cu увеличивают агломерацию нанопленок и, как следствие, их намагниченность и коэрцитивную силу. Хотя, отжиг смачивающего слоя Cu, уменьшает степень прямоугольности петли магнитного гистерезиса.

Ключевые слова: многослойные пленки, смачивающий слой, рост, агломерация, морфология, металлы, кремниевая подложка, петля гистерезиса, атомно-силовая микроскопия, магнитооптический эффект Керра

Ссылка при цитировании: Плюснин Н. И., Усачев П. А., Павлов В. В. Влияние толщины и отжига смачивающего слоя Si(001)2×1-Cu на морфологию слоистых нанопленок на основе Fe, Co, и Cu и их ферромагнитные свойства // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.1. С. 131–136. DOI: https://doi.org/10.18721/ JPM.153.122

Introduction

In recent years, considerable attention has been paid to developing spin transistors and spin injectors using spin valves made of multilayer metal nanostructures based on ferromagnetic metals and their alloys [1]. Such nanostructures should have high spin conductivity, degree of polarization, magnetization, and Curie temperature. To increase the spin conductivity, it is suggested to place these nanostructures on top of an intermediate layer of an inert noble metal on a substrate [2]. Additionally, it is proposed to use layered composite nanomaterials from a ferromagnetic metal and a noble metal [3]. Therefore, the study of the influence of intermediate layers of noble metals (Cu) or their wetting layers on the growth, morphology, and magnetic properties of multilayer metal nanostructures on silicon is topical for spintronics.

From a physical point of view, the fundamental interest is a multilayer structure made of dissimilar metals on an alien (silicon) substrate. It is important to understand what phenomena occur during the growth of this structure and how are they related to the growth phenomena of the first wetting layer. In addition, it is important to clarify how the combination of a magnetic transition metal and a noble non-magnetic metal will affect the growth of a multilayer film and its magnetic properties. In this work we try to clarify these questions.

It can be expected that the difference between layers of different nature and degree of reactivity, which wet the substrate to different degrees, can have different effects on the growth of a multilayer film and its morphology. Thus, we can expect a significant morphological dependence on the type of the first metallic film on silicon. On the contrary, the growth of metal on metal may have a weaker morphological dependence on the type of the first metal. However, in general, the film morphology should significantly affect its magnetic properties.

Previously, we studied the growth of ultrathin and atomically smooth layers and films of Cu (1–5 ML) [4], Fe (10–25 ML) [5, 3], and Co (10 ML) [6] on silicon. A technology for their growth was based on a decrease in the temperature of steam in sources during the formation of a wetting layer (see [4–8]). Multilayer nanofilms based on Fe, Co, and Cu were also prepared [3]. However, the morphology of these films, its relation to film production conditions, and the effect on magnetic properties were not studied yet.

Here we present the growth and study of Fe (10–12 ML) and Cu (8 ML)/Fe(16 ML)/Cu (5 ML)/Co(10 mL) multilayer nanofilms on an intermediate two-dimensional layer of Cu (1–2 mL), which plays not only the role of a wetting layer but also that of a buffer layer blocking the formation of compounds or alloys between the overlying and underlying layers. Moreover, two-dimensional layers of noble metals simultaneously play the role of a highly conductive transport layer, which increases the longitudinal conductivity of a two-layer or multilayer nanofilm. The purpose of this study is to determine the effect of the thickness and annealing of a two-dimensional wetting layer on the morphology and magnetic properties of multilayer nanofilms in order to determine the optimal modes for their production as spin injectors.

Experiment

Samples were prepared in a microwave chamber with RIBER analyzers for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) electron energy loss spectroscopy (EELS). The chamber was equipped with a sample manipulator, a quartz microbalance, as well as molecular beam (ribbon) sources of Fe, Co, and Cu, and other equipment (see [3]).

Metal layers were deposited on silicon at room temperature of the Si(001) substrate and at a low temperature of metal vapors. They were deposited on a Si(001)-2×1-Cu wetting layer (1–2 ML thick) before and after its annealing at 250°C. The thickness of the wetting layer corresponded to the formation of a phase of average composition Cu2Si [5] and was in the range of 1–2 ML.

Phosphorus-doped single-crystal silicon wafers were used as substrates. They had a size of 20×5 mm^2, a thickness of 0.42 mm, orientation (001) and a resistivity of 4.5 Ω·cm. The Si wafers were preliminarily cleaned with organic solvents and then loaded into a degassed ultrahigh vacuum chamber with a base pressure of 5×10^{-10} Torr. After that, the Si wafers were heated at a temperature of 600 °C for several hours. Before the first deposition of metal on a clean Si surface, the temperature of the Si wafers was raised to 1250 °C and then gradually lowered to room temperature, quickly passing the temperature range of about 1000 °C.

The crystallographic quality of the prepared surface of the Si(001)-2×1 silicon substrate was controlled by the presence of sharp and bright 2×1 reflections in the LEED pattern. Surface cleanliness was monitored by the presence of oxygen and carbon peaks in the AES. The temperature of the Si substrate was set by passing a constant electric current through it.

Metal vapors were deposited on the substrate by thermal sublimation of metals from Cu, Co, and Fe films preliminarily deposited onto a Ta tape 5×25 mm^2 in size and 10–20 μm thick. These films were deposited using evaporation from Fe or Co rods placed inside a tungsten coil or from a drop of Cu formed on a V-shaped tungsten wire. All metals had more than 99.98% pure. The metal vapor temperature (T_{Fe} =1250 ºC, T_{Co} = 1130 ºC and T_{Cu} = 900 ºC, $\Delta T < \pm$ 5 ºC) was maintained by passing a direct electric current through tungsten tape or wire heaters. Simultaneously, deposition was carried out on two samples, while the distance from the tape source to the Si substrates was about 2 cm.

Magnetic characteristics of the samples were studied in longitudinal geometry using an experimental setup based on the magneto-optical Kerr effect (MOKE). The light source used in the MOKE studies was a helium-neon laser with the wavelength of 632 nm and whose light intensity was modulated at a frequency of 42 kHz. A PEM-100 photo-elastic modulator from Hinds Instruments was used for modulation, and an SR830 lock-in amplifier from Sanford Research was used for signal detection. The sensitivity to the rotation angle of the polarization plane was about 1 second of arc.

AES and EELS spectra were recorded using low electron energy (300 eV). This made it possible to ensure high sensitivity of the spectra in the film thickness range of 1–10 ML, as well as sensitivity to the state of the interface at a film thickness of 0–3 ML. To obtain LEED images, electron energies were used in the range of 50–100 eV, which ensured a probing depth of about 1 ML. Quantitative analysis of AES was performed with an error of ~20%, taking into account the accuracy of determining the probing depth in the literature. The AFM data were acquired in semi-contact scanning mode on an NT MDT Silver-47 microscope and processed using standard software from NT MDT.

Results and Discussion

The LEED images show that a partial attenuation of the 2×1 reflections occurred after deposition of 1 ML and 2 ML Cu on Si(001)-2×1. However, the 2×1 reflections became brighter after 1st ML annealing, showing the formation of a two-dimensional layer with a 2×1 structure. Complete attenuation of the reflections occurred after the deposition of 3 ML or its annealing, which indicates the growth of a continuous Cu layer with a subcrystalline (cluster) structure.

According to changes in the intensity of Cu, Fe, and Co Auger peaks, after the formation of the Cu (WL) wetting layer, pseudolayered growth of Co (Fe), Cu, Fe, and Cu and Si segregation occurred. The last Si layer was apparently forced out of the substrate during film growth.

The formation stages of surface and bulk plasmonic peaks of Fe and Co losses in EELS also corresponded to pseudolayered growth. However, for Fe and Co on Cu, a slower growth was observed, which indicates film agglomeration and the growth of Fe and Co islands.

The AFM data directly showed film agglomeration in all samples. As can be seen from Fig. 1, the average relief height was in the range of 1–12 nm and, depending on the presence and annealing of the Cu wetting layer, increased by a factor of 1.2–1.5 in the case of an Fe nanofilm and by a factor of 2 in the case of multilayer films. At the same time, the lateral size of grains in the samples and their number decreased.

Since the morphology of the entire multilayer film as a whole is given by the morphology of the first ferromagnetic layer (Co, Fe), it can be concluded that the presence of Cu-WL leads to agglomeration of this first layer. However, as the next layers grow, additional agglomeration occurs and grains of similar sizes are formed (Fig. 1, *c, f*).

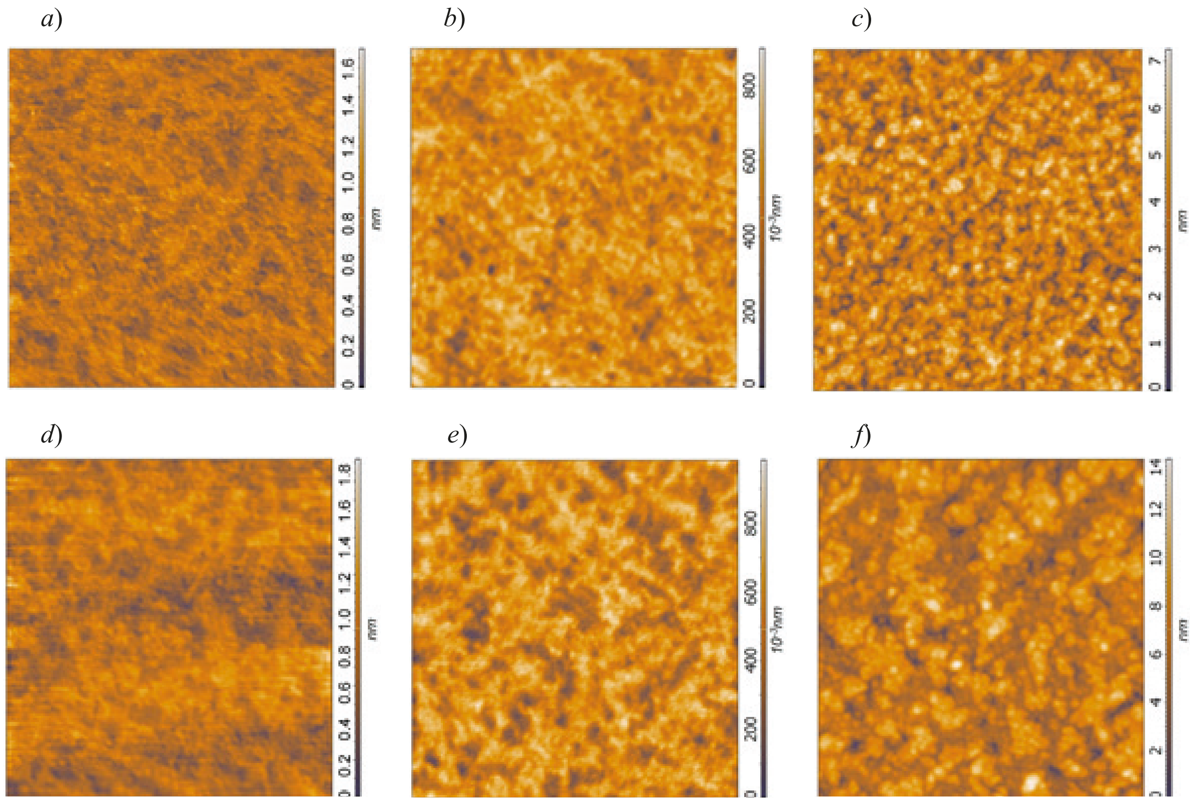

Fig. 1. AFM images (1000×1000 nm[2]) of Fe (*a, b, d, e*) nanofilms with a thickness of 10–12 ML and Cu/Fe/Cu/Co multilayer (*c, f*) with a total thickness of 39 ML grown on Cu WL, respectively, 1 and 2 ML thick: without pre-annealing (*a, b, c*), subjected to annealing (*d, f*), with Cu WL thickness increasing from 1 ML (*b*) to 2 ML (*e*)

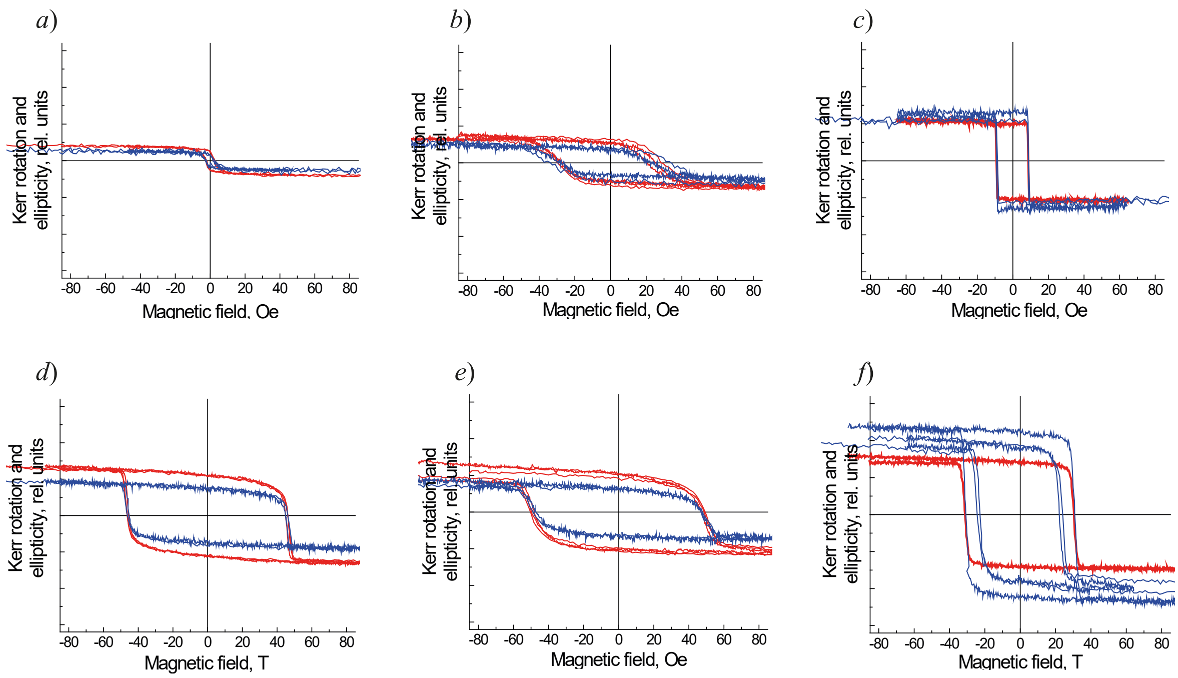

Fig. 2. Longitudinal Kerr rotation (red) and ellipticity (blue) in Fe (*a, b, d, e*) nanofilms with a thickness of 10–12 ML and Cu/Fe/Cu/Co multilayer (*c, f*) with a total thickness of 39 ML grown on a Cu WL respectively, 1 and 2 ML thick: without pre-annealing (*a, b, c*), subjected to annealing (*d, f*), with Cu WL thickness increasing from 1 ML (*b*) to 2 ML (*e*)

When a non-magnetic metal (Cu) is grown on a wetting layer and annealed, the multilayer film composed of Cu/Fe/Cu/Co layers becomes looser and consists of larger islands (Fig. 1, *d, e, f*). In this case, the coercive force and magnetization in the obtained nanofilms become much higher (Fig. 2, *d, e, f*) than without the interlayer and its annealing (Fig. 2, *a, b, c*). At the same time, generally, increased values of the coercive force are observed, which cannot be explained only by a change in the type of metal or morphology. Since, according to the AES data, Si solid solutions are formed in the grown layers, the presence of Si in the Fe and Co layers increases the coercive force.

In general, the observed phenomena have the following explanations. When a metal is deposited on a clean silicon surface, a 2D wetting layer grows, a 3D metastable phase grows, and then a 3D stable bulk metal phase grows [4–5, 8]. At the same time, the 2D-3D transition causes the separation of a small amount of silicon from the substrate and the segregation of silicon atoms (the thickness of the segregated layer is less than the monolayer). At the last stage of growth (when a stable bulk metal phase is formed), the precipitated Si dissolves in the growing metal film. Meanwhile, without an intermediate Cu layer, the formation of silicide and the dissolution of Si suppress the ferromagnetism of the multilayer film.

At the same time, these processes are blocked for wetting with copper, and ferromagnetism becomes more pronounced. Obviously, wetting with copper leads to an increase in the degree of agglomeration of ferromagnetic layers caused by the chemical inertness of copper. In addition, the presence of an intermediate wetting metal layer (Cu) blocks the mixing of the ferromagnetic metal with silicon during its pseudolayer (multi-island) growth. However, during annealing, the Cu layer is partially collected into islands near the substrate steps. This leads to a concentration of multi-island growth on the terraces and the film becomes less continuous.

In both cases, the nanofilm on the Cu wetting layer collects into islands more strongly than when grown on a clean surface of a silicon substrate. As for the growth of intermediate (between ferromagnetic layers) and upper layers of Cu, it proceeds in accordance with the pseudolayer-by-layer growth mechanism, since the Cu layers spread well over the surface of the ferromagnetic metal. In addition, the Cu layers increase the mobility of atoms in the film and help even out the shape of the agglomerates. The subsequent growth of the ferromagnetic metal on Cu also occurs in accordance with the pseudolayer growth mechanism, but is accompanied by an increase in agglomeration. Finally, the last noble metal layer (Cu) spreads over the film again and evens out the shape of the agglomerates.

As can be seen from Figure 2, the larger the diameter and height of the agglomerates, the more pronounced the ferromagnetic properties (magnetization and coercive force) become. This corresponds to the well-known data on the relationship between the sizes of crystals and their magnetic properties (see, for example, [9]). However, as can be seen from Figure 2, *c*, the squareness of the hysteresis loop is obviously more pronounced if there are ferromagnetic grains of the same size, as happens in the case of an unannealed wetting layer. In addition, saving the thickness of the ferromagnetic layers leads to an exchange interaction between the layers and to the formation of the smallest coercive force (coercive force Co) between the two ferromagnetic layers.

Conclusions

- Ultrathin layers of Cu on silicon with a thickness of 1–2 monolayers with and without annealing were prepared, which were used as a wetting and buffer layer for the subsequent growth of ferromagnetic layers of Fe and Co.
- The effect of wetting layer annealing and its thickness on the morphology of layered nanofilms on silicon with ferromagnetic (transition metals Fe and Co) and nonmagnetic (noble metal Cu) layers is shown.
- The degree of agglomeration and grain size in multilayer nanofilms have a decisive influence on the magnetic properties (magnetization and coercive force) of the obtained nanomultilayers.
- Optimum nanofilms for spin valves, in terms of magnetization strength, are nanofilms that are grown with annealing of the Cu wetting layer, and in terms of a more rectangular hysteresis loop and a narrower hysteresis loop, those that are grown without annealing.

REFERENCES

1. **Plusnin N.,** Creation of electrical spin injectors for silicon spintronics: Achievements and prospects. Solid State Phenomena. 245 (2016) 32–41.
2. **Zavaliche F., Wulfhekel W., Xu H., Kirschner J.,** Suppression of silicide formation in Fe films grown on Si (001). Journal of Applied Physics, 88 (9) (2000) 5289–5292.
3. **Plyusnin N. I., Il'yashchenko V. M., Usachev P. A., Pavlov V. V.,** Growth and structural and magnetic properties of multilayer Fe, Co, and Cu nanofilms on silicon. Technical Physics, 60 (10) (2015) 1501–1507.
4. **Plyusnin N. I., Ilyashchenko V. M., Kitan S. A., Tarima N. A.,** Structural-phase transformations at the initial stages of copper condensation on Si(001). Surface. X-ray, synchrotron, and neutron studies (RU). (8) (2011) 29–40.
5. **Plyusnin N. I., Ilyashchenko V. M., Kitan S. A., Krylov S. V.,** Formation, electronic structure, and stability of transition metal film nanophases on silicon. Surface. X-ray, synchrotron and neutron studies (RU), (9) (2009) 86–98.
6. **Plusnin N. I., Il'yashenko V. M., Kitan S. A., Krylov S. V.,** Formation of Co ultrathin films on Si (1 1 1): Growth mechanisms, electronic structure and transport. Applied surface science, 253 (17) (2007) 7225–7229.
7. **Plyusnin N. I., Ilyashchenko V. M., Krylov S. V., Kitan S. A.,** Influence of the power carried by an atomic beam on the formation of the Fe/Si (111) 7x7 interface. Letters to ZhTF (RU), 33 (11) (2007) 79–86.
8. **Plusnin N. I., Il'iashchenko V. M., Krylov S. V.,** Metal thin-film nanophases and their interface with silicon. In Journal of Physics: Conference Series. 100 (5) (2008) 052094.
9. **Qiu Z. Q., Bader S. D.,** Surface magneto-optic Kerr effect (SMOKE). Journal of magnetism and magnetic materials, 200 (1–3) (1999) 664–678.

THE AUTHORS

PLYUSNIN Nikolay I.
plusnin@dvo.ru
ORCID: 0000-0001-9691-9721

PAVLOV Viktor V.
pavlov@mail.ioffe.ru
ORCID: 0000-0001-6139-6123

USACHEV Pavel A.
usachev@mail.ioffe.ru
ORCID: 0000-0002-1386-6466

Received 29.05.2022. Approved after reviewing 29.06.2022. Accepted 29.06.2022.