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Physical deposition of atomic layers and growth of extremely thin films: four-decade series of the refractory metal-silicon system studies

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Abstract. The article is devoted to the author's four-decade series of studies on growing extremely thin films (ETF) in the refractory metal-silicon system. To obtain ETF, it was necessary to develop a new growth method — physical atomic-layer deposition (PALD), which uses the technique of pulsed evaporation of adsorbate from a flat source located parallel to the substrate. Compared to the traditional molecular beam deposition (MBE) method, PALD reduces the vapor temperature, produces thinner layers, and expands the range of materials produced. The study showed that, with PALD using reduced substrate and vapor temperatures, not only two-dimensional surface phases (2D-SP) can form, but also two-dimensional (2D-SWL) and, subsequently, nanophase (ν-SWL) wetting layers (SWL). The series investigated the growth of ETFs Cr, Co, Fe, Cu and their silicides on Si(111) and Si(001), as well as the growth of Si on Si(111)7×7 and $CrSi_2$(0001). Single-layer and multilayer (Co-Cu-Fe-Cu) nanofilms were obtained. The main causes of phase transitions in SWL have been identified, and the role of vapor pressure and substrate temperatures in the structure and composition of SWL and the boundary layer of the substrate has been shown. The study showed that the films obtained by the PALD method have unique electrical, optical and magnetic properties and are promising for use in micro- and nanoelectronics nanodevices.

Keywords: atomic-layer deposition, surface phases, wetting layers, phase transitions, extremely ultrathin films, multilayer nanolayers, Cr, Co, Fe, Cu, silicides, Si(111) and Si(001), electrical, optical and magnetic properties

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Материалы конференции
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Физическое осаждение атомных слоев и рост предельно-тонких пленок: сорокалетняя серия исследований системы тугоплавкий металл-кремний

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Аннотация. Статья посвящена сорокалетней серии исследований автора по выращиванию экстремально-тонких пленок (ETF) в системе тугоплавкий металл-кремний. Для получения ETF необходимо было разработать новый метод роста — физическое атомно-слоевое осаждение (PALD), использующее технику импульсного испарения адсорбата из плоского источника, расположенного параллельно подложке. По сравнению с традиционным методом молекулярно-лучевого осаждения (MBE), PALD позволяет снизить температуру пара, получить более тонкие слои и расширить ассортимент получаемых материалов. Исследование показало, что, при PALD, использующем пониженные температуры подложки и пара, могут образовываться не только двумерные поверхностные фазы (2D-SP), но и двумерные (2D-SWL) и, затем, нанофазные (ν-SWL) смачивающие слои (SWL). В серии был исследован рост ETF Cr, Co, Fe, Cu и их силицидов на Si(111) и Si(001), а также рост Si на Si(111)7×7 и $CrSi_2$(0001). Были получены однослойные и многослойные (Co-Cu-Fe-Cu) нанопленки. Были выявлены основные причины фазовых переходов в SWL, а также показана роль давления, температур пара и подложки в структуре и составе SWL и пограничного слоя подложки. Исследование показало, что полученные методом PALD пленки, обладают уникальными электрическими, оптическими и магнитными свойствами и перспективны для использования в наноустройствах микро- и наноэлектроники.

Ключевые слова: атомно-слоевое осаждение, поверхностные фазы, смачивающие слои, фазовые переходы, предельно-тонкие пленки, многослойные нанослои, Cr, Co, Fe, Cu, силициды, Si(111) и Si(001), электрические, оптические и магнитные свойства

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Introduction

The fundamental basis for growing nanostructures of micro- and nanoelectronics is knowledge about the initial stage of thin film growth and the formation of its interface. This stage, in fact, is the formation of the elemental and phase composition, structure and morphology of 2D-SP, SWL, ETF and their interface with the substrate. However, it was only 30 years after the publication of our first papers [1, 2] that it became obvious (see below) that the thin-film phase (TP), which forms after 2D-SPS and before the growth of the first ETF layer, is an SWL in the form of first two-dimensional (2D-SWL) and then nanophase (ν-SWL) layer.

Historically, up to a certain stage, two approaches to ETF growth existed independently and moved towards each other: “approach I” – from three-dimensional massive phases (3D-BP) to ETF and “approach II” – from 2D-SP to ETF. In these approaches, the understanding of the nature of 2D-SP and SWL was influenced by differences in research methods, in particular, the degree of microscopicity of these methods. For example, the use of optical methodologies such as ellipsometry has led to the conceptualization of SWL as a metastable 3D-BP [3]. Conversely, the use of surface-sensitive techniques [4] led to the identification of exclusively interphase boundary phase [5] or 2D-SP [6, 7] with their own composition, thickness, density, and lattice [4]. A more complete understanding of the nature of SWL was obtained later (see below).

Based on a review of forty years of research on the cultivation of ETFs metals (Me) and their silicides (MSix) on silicon or silicon on Si or $MeSi_x$ substrates, this article presents a new perspective on ETFs formation. The results of these studies are systematized in chronological order in accordance with the developed theory of ETF growth within the framework of approach II developed by the author.

Chronological overview

In the very first works [1, 2], TP spectra were obtained by electron energy loss spectroscopy (EELS), which demonstrated a reduced electron density in TP compared to that in 3D-BP. In this study, TP was identified as a low-dimensional phase, called “atomically similar” because of its low density. However, this TP had a thickness of several monolayers (> 3 ML), which is not typical for 2D-SP. Therefore, the authors of [1, 2] attributed it to a kind of “increased thickness” SP, implying that this “thick” SP, like the “submonolayer” 2D-SP, is stabilized by the substrate.

Subsequent studies focused on the mixing of Me-Si at low temperatures and its role in the formation of TP and ETF. Studies in the Si(111)-Cr system have shown that mixing and formation of mixed TP plays a significant role in the formation of both ordered and disordered ETF of silicides [1, 2, 8–10]. The data obtained was systematized in the form of a diagram describing the conditions for the formation of Cr-Si TP and $CrSi_2$ ETF [10]. These results showed thickness and temperature that determines the transition from 2D-TP to 3D-TP with increased thickness and two types of “patterns” of the $CrSi_2$ ETF, A- or B-type, with an azimuthal angle relative to Si(111) of 0° and 30°. The use of the appropriate TP and template made it possible for the first time to produce a epitaxial $CrSi_2$ A-type film with a thickness of 1000 Å and an increased carrier mobility.

It should be noted that these early studies were conducted at elevated steam temperature and reduced steam pressure (excluding the experiment [1, 2]). However, a number of studies of Cr-Si(111), Co-Si(111), and Si-$CrSi_2$(0001) systems have demonstrated that increasing vapor pressure (deposition rate) reduces mixing. To explain this phenomenon, a computer simulation cycle of growth kinetics was initiated. This modeling culminated in a probabilistic geometric analytical model of growth kinetics, which clarified the role of increasing vapor pressure in the aforementioned transition from mixing to growth [11]. Subsequent studies focused on the growth of amorphous Si on Si(111), the role of mixing in the formation of Co ETFs on Si(111), and the growth of amorphous TP and epitaxial Si ETF on $CrSi_2$(0001) [12].

However, to avoid mixing and reduce the thickness of the ETF, increased pressure or a lower vapor temperature was required. It was necessary to develop a technique for producing steam that would ensure either its high pressure or its low temperature. For this purpose, a deposition technique was developed [12] based on the previously known “hot wall” technique. This technique (double deposition) provided first pulsed deposition of adsorbate on a cold wall (secondary source), and then from this heated wall onto a cold substrate [13].

This innovative approach has led to the successful cultivation of TP and ETF containing almost pure Me (Si solid solution in Me) [12, 14]. It is noteworthy that “pseudo-three-dimensional” ν-TP have been identified, exhibiting nanoscale heterogeneity similar to that of known bulk nanophases (ν-phases) [15, 16]. The research cycle was completed by summarizing the results of [17] and investigating the role of steam temperature [18]. Subsequent studies focused on the growth of Cu-Si TP and Cu_3Si ETF, as well as layered ETF containing Co, Fe and Cu. The first generalization of these and previous results with the interpretation of TP as solid-phase wetting layers (SWL) was made in reviews [19–21]. The final period in the research series was associated with the formation of the SWL (or WL) concept [20]. In the review papers [21], the unique properties of the obtained nanostructures and potential applications in nano- and microelectronics were described. These include: nanocontacts or interconnects, electrodes and channels of field-effect (FET) and spin transistors, translucent contacts for infrared (IR) and ultraviolet (UV) sensors, cores for electromagnetic sensors, layers of spin filters and many other applications.

After that, experiments on SWL growth have been conducted and a phenomenological theory of its origin and growth has been developed (see references in [22–25]). Then SWL modeling has been performed for a number of Me-Si systems [26–29]. Recent first-principle modeling has shown that the main mechanism of the transition from SWL to ETF is a change in the coordination of atoms and electronic structure in SWL with increasing thickness, which leads to stress accumulation and atomic rearrangement in the film and the boundary layer of the substrate, and then to the destabilization of the film-substrate system and the transition of SWL to 3D-BP (ETF), accompanied by the release of latent energy in the form of heat.

Conclusion

This paper presents a series of studies devoted to the growth of extremely thin films from the vapor phase in a metal-silicon system. The role of a solid wetting layer in this process is demonstrated, and the fundamental causes of this phenomenon are discussed. A new growth method, physical atomic-layer deposition (PALD), has been developed through pulsed evaporation of an adsorbate from a flat source positioned parallel to the substrate. This significantly reduced the vapor temperature in atomic streams and allowed for control of film thickness and composition. PALD has been used to produce extremely thin and nanofilms of refractory metals (Cr, Co, Fe) on silicon. These films possess a unique structure, electrical, optical, and magnetic properties, and hold promise for the development of micro- and nanotechnologies.

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