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IR SPECTRA OF THIN FILMS PRODUCED BY THE ION-PLASMA METHOD

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Annotation: Thin films play an important role in modern technologies. They are successfully used, especially in the rapidly developing fields of electronic technology and light engineering, in the construction industry, including integrated microcircuit technologies; as anti-corrosion, decorative, filtering and radiation redistributing coatings.

We have successfully grown manganese silicide films using an ion plasma method under high vacuum conditions using a magnetron sputtering device. Thin manganese silicide films (Mn_4Si_7/glass and SiO_2/Si) produced by the "ion-plasma" method were taken as the research object.

The thickness of the thin films and the mean noise limits and standard deviation were measured on an IRTracer-100 spectrophotometer.

Keywords: ion-plasma method, spectrophotometer, thin films of manganese silicide, absorption and transmission spectra

ИК СПЕКТРЫ ТОНКИХ ПЛЕНОК, ПОЛУЧЕННЫХ ИОННО-ПЛАЗМЕННЫМ МЕТОДОМ

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Аннотация: Тонкие пленки играют важную роль в современных технологиях. Они успешно применяются, особенно в бурно развивающихся областях электронной техники и светотехники, в строительной индустрии, в том числе в интегральной микросхемостроительной технике; в качестве антикоррозионных, декоративных, фильтрующих и радиационно-перераспределяющих покрытий.

Мы успешно вырастили пленки силицида марганца ионно-плазменным методом в условиях высокого вакуума с использованием устройства для магнетронного распыления. В качестве объекта исследования были взяты тонкие пленки силицида марганца (Mn4Si7/стекло и SiO2/Si), полученные «ионно-плазменным» методом.

Толщину тонких пленок, средние пределы шума и стандартное отклонение измеряли на спектрофотометре IRTracer-100.

Ключевые слова: ионно-плазменный метод, спектрофотометр, тонкие пленки силицида марганца, спектры поглощения и пропускания

Introduction. An important requirement for thin-film materials is the preservation of their properties and structure for a long time. At present, the requirements for thin-film materials are increasing, which is due to the consumer ability of a rapidly developing industry. In this regard, materials in the thin-film state must have a number of physicochemical and operational properties [1]. Modifications of composite thin-film materials are used in a wide range of areas of microelectronics, electrical engineering, space technology, mechanical engineering, and the construction industry [3, 5].

Using a molecular turbopump (Pfeiffer vacuum), a high vacuum was created in the chamber of the EPOS-PVD-DESK-PRO magnetron device at a pressure of 10^{-6} Torr. By introducing gaseous argon into the chamber, a pressure sufficient to create an ion-plasma system was created, and this process was controlled on the SR-307 monitor of the Manetron device. First, a clean glass plate was subjected to mechanical cleaning with hydrofluoric acid diluted by 20 % to remove surface oxide, then the glass surface was re-cleaned by ionization of argon gases inside the chamber using an "ion-plasma" processing device installed in the magnetron chamber.

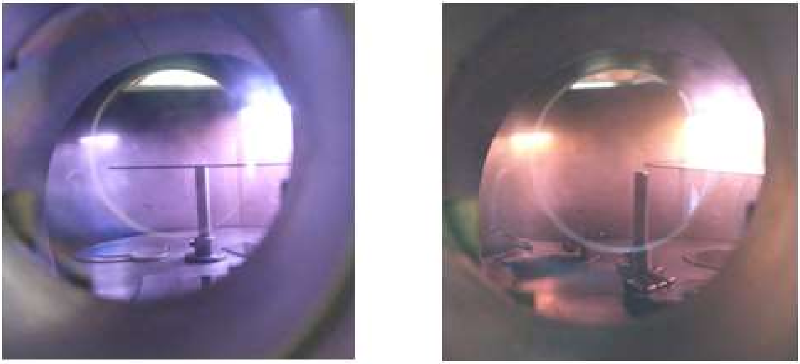


Figure 1 – Formation of nanofilms by the "ion-plasma" method on the magnetron installation EPOS-PVD-DESK-PRO

The current from the power source of the magnetron was 657 mA, power 221 W, voltage 336 V. Air was sucked into the chamber until a pressure of 10^{-5} Torr was reached using a turbopump. First, thin films of manganese silicide of various thicknesses were created at room temperature, at a pressure of $8 \cdot 10^{-4}$ mbar by the ion-plasma method. The absorption and transmission spectra of the films obtained by the ion-plasma method were obtained on an IRTracer-100 spectrophotometer using the Happ-Hanzel method.

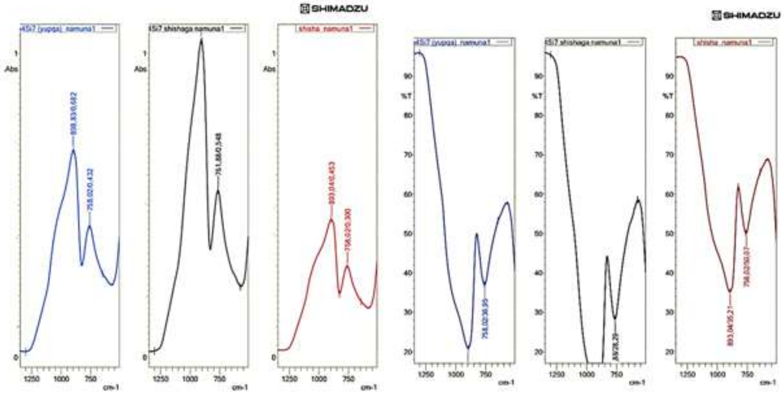


Figure 2 – Absorption and transmission spectra of Mn_4Si_7 nanofilms of various thicknesses

A number of smoothing and editing functions are used to obtain absorption and emission spectra in the functional FT-IR measurement device [2].

The transmission spectrum results obtained from the FT-IR spectroscopy measurement of a glass substrate are presented in Table 1 below.

Table 1 – Results of glass in the infrared region of 600-15500 cm^{-1}

№	**Peak sm^{-1}**	**Intensity %**	**Absor**	**Corr. Intensity**	**Base (H) sm^{-1}**	**Base (L) sm^{-1}**	**Corr. Area**
1	758,02	50,07	0,300	0,59	761,88	644,22	-42,439
2	893,04	35,21	0,453	0,77	894,97	825,53	192,278

Tables 2 show the results of the transmission spectra of FT-IR spectroscopy of thin films of manganese silicide (Mn_4Si_7) formed on glass by the ion-plasma method at various thicknesses.

Table 2 – Results of Mn_4Si_7 in the infrared region of 550-1200 cm^{-1}

№	Peak sm^{-1}	Intensity %	Absor	Corr. intensity	Base (H)	Base (L)	Corr. Area
1	758,02	36,95	0,423	0,29	759,95	648,08	-37,596
2	761,88	28,29	0,548	0,31	763,81	574,8	-480,671
3	898,83	20,78	0,682	0,83	1300,02	894,97	1133,76
4	904,61	9,01	0,863	0,51	1300,1	902,7	1083,47

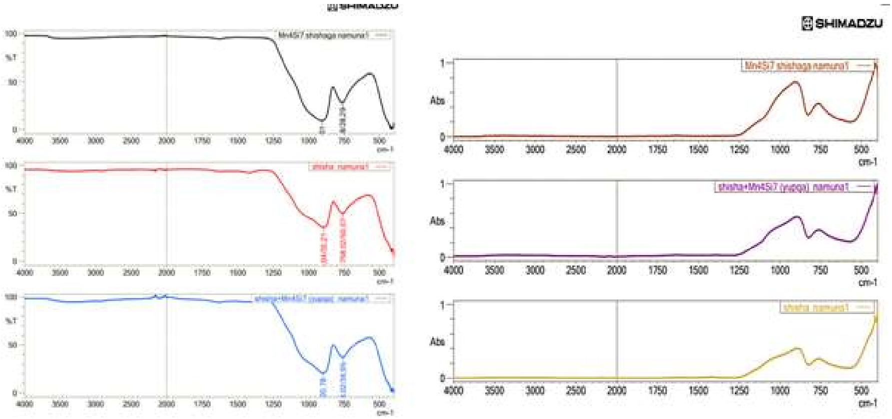


Figure 3 – The general view of the transmission and absorption spectra of films obtained with different thicknesses is described

In the data processing section of the IRTracer-100 spectrophotometer, in the “Film thickness” function, knowing the angle of incidence and refractive index, one can measure the film thickness, the number of average interference thresholds and the standard deviation [6]. Table 4 below shows the measured parameters of films of various thicknesses obtained in the Magnetron device.

Table 3 – Measured mean noise limits, standard deviation, and layer thickness for Mn_4Si_7

Sample name	Refractive index	Incident angle	Average interference fringes	Thickness	Standard deviation
glass	1,5560	45,00	115	122,67 um	214,96 um

Sample name	**Refractive index**	**Incident angle**	**Average interference fringes**	**Thickness**	**Standard deviation**
Mn_4Si_7/glass (thin)	1,5700	45,00	102	108,92 um	247,19 um
Mn_4Si_7/glass (thick)	1,5700	45,00	74	78,89 um	136,83 um

The obtained spectra were compared with the literature of the "Shimadzu Standard Library". If the previous results were measured in the range of 600÷4000 cm^{-1}, then our results were measured in the range of 400÷4000 cm^{-1}. This indicates the possibility of the IRTecer-100 spectrophotometer of the latest model [2]. For us, this is the most important, because semiconductors create the main peaks in the region of 400÷600 cm^{-1} of infrared radiation.

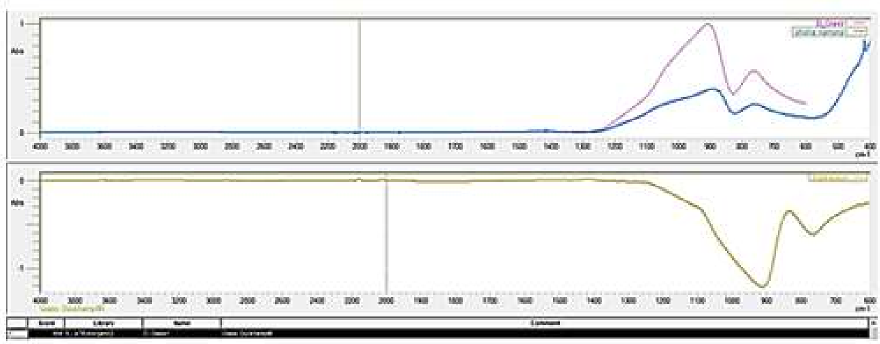
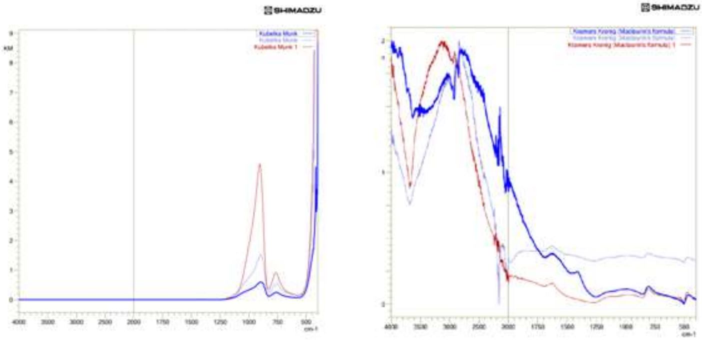


Figure 4 – Absorption spectrum of the Mn_4Si_7/glass film compared to the "Shimadzu Standard Library" and the spectrum of the obtained substrate mixture

Finding optical constants using Fourier spectroscopy today improves the accuracy of research results. In our article, we also studied the refractive indices, transmission and absorption coefficients, and other film constants from the Kubelka-Munk and Kramers-Kroing relations.



a b

Figure 5 – Figure:
a) Kubelka-Munk spectrum of manganese silicides of various thicknesses;
b) Kramers-Kroing spectrum

Figure 6 shows the transmission and absorption spectra of the $SiO_2/Si(111)$ film in the range 400÷4000 cm^{-1}, with water vapor (H_2O) or carbon dioxide (CO_2) in the spectra of molecules undergoing the following adjustments to reduce the effects: addition, smoothing, zero correction of the baseline, normalization, filtration and ATR correction.

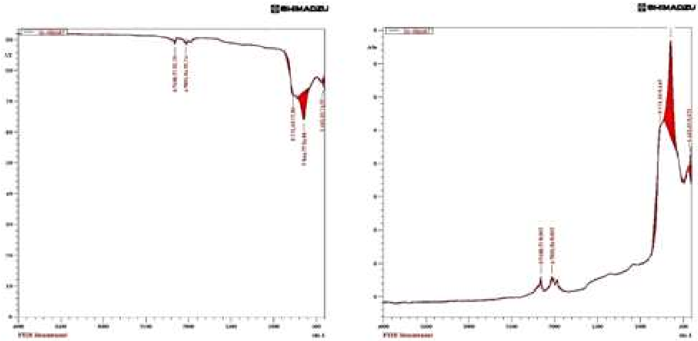


Figure 6 – Smothing analysis of the transmission and absorption spectrum of $SiO_2/Si(111)$

When silicon is oxidized (naturally, in the atmosphere of air or under the influence of high temperatures), Si-OH hydroxyl groups are formed on its surface, and siox groups are formed in the near-surface layer. The presence of hydroxyl groups leads to adsorption of atmospheric moisture and corresponding changes in the spectra of samples [7].

Figure 6 shows the infrared absorption and transmission spectra of the SiO_2 film formed on the silicon surface. In the absorption spectrum, the peak was observed in the region of 769.60 cm^{-1}. These lines correspond, respectively, to antisymmetric stretching oscillations of Si-O-Si groups. The peak of the transmission spectrum in the region of 644.22 cm^{-1} corresponds to the “fingerprint" region of the pure silicon spectrum. Silicon dioxide layers have three absorption zones: a low-frequency band of 418.55 cm^{-1}, a weak band of 771.53 cm^{-1} and an intense broadband band with a maximum of 644.22 cm^{-1}. These lines relate to the oscillations of the pendulum, symmetric stretching and antisymmetric stretching of Si-O-Si groups, respectively. Depending on the brittleness of the oxide, the final strip can have a half width from ≈ 95 cm^{-1} to $\approx$ 140 cm^{-1} for dense oxide. While studies of silicon oxides have shown that SiO_x ($x=1\div2$) is formed during deposition and annealing, with a decrease in *x*, the maximum boundary of the *n* band (SiOSi) shifts to the region of lower wave numbers (915 cm^{-1} at x=1, 980 cm^{-1} at x=2). The frequency, on the contrary, increases from 780 to 835 cm^{-1}; the frequency of oscillation of the pendulum increases with increasing x [8].

Table 4 – Results of SiO_2/Si thin film in the infrared region

No	Peak sm^{-1}	Intensity %	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	418,55	0,125	0,014	428,20	410,84	2,049	0,111
2	644,22	0,194	0,058	725,23	572,86	24,347	3,597
3	771,53	0,142	0,003	866,04	767,67	9,744	-0,491
4	2031,04	0,052	0,002	2038,76	2023,33	0,786	0,019
5	2160,27	0,052	0,005	2167,99	2150,63	0,854	0,038

In the case of thin films, infrared interference spectra carry information about the anisotropy of the material and make it possible to determine the refractive index and rotation of molecules located in the IR region of the spectrum [9].

Conclusion. There are many factors affecting the material parameters of thin films, such as the moderation of the production environment, crystal size and controlled orientation, film uniformity, etc. The electrical and optical properties of films obtained by the "ion-plasma" method, one of the most modern methods, have been studied. obtaining thin films. As the film thickness increases, the transmission of infrared radiation decreases, and it can be observed that the wave number of the maximum peaks shifts to the short wavelength side. As the thickness of the film increases, the transmittance of infrared radiation decreases, and the wavenumber of the maximum peaks is observed to shift towards shorter wavelengths. The effect of oxygen on silicon was studied. It can be concluded that Mn4Si7 has a semi-metallic nature. The main fluctuations changed in the range of wave numbers 983.04 ÷ 904.61 cm^{-1}. This corresponds to photon energies of 0.1124÷0.1223 eV.

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