Influence of Surface Geometry on Metal Properties

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Abstract

The influence of surface geometry on metal properties is studied within the limit of the quantum theory of free electrons. It is shown that a metal surface can be modified with patterned indents to increase the Fermi energy level inside the metal, leading to decrease in electron work function. This effect would exist in any quantum system comprising fermions inside a potential energy box.

Introduction

Recent development of such technologies as electron beam milling and ion beam lithography enable the fabrication of structures with dimension as small as a few nanometers. Those low dimensions are comparable with the de Broglie wave length of a free electron inside the metal. Because of this, it has become possible to fabricate some microelectronic devices [1-2] working from the wave properties of the electrons.

In this Letter I will discuss what happens when regular indents, influencing free electron de Broglie waves, are etched into the surface of a metal.

In the beginning I will review the well-known case of a fermion inside the potential energy box, and I will investigate how the modification of the geometry of the boundary of potential energy box will affect the boundary conditions for the particle wave function, and the resulting solutions for Schroedinger's equation. Next, the behavior of fermions inside this potential energy box will be studied. The results will be extrapolated to the particular case in which the fermion is an electron and the potential energy box is a metal. It will be shown that modification of the metal's surface will lead to a increase of Fermi energy level, with a resulting decrease of the work function of the metal.

Finally, the experimental possibility of the fabrication of such indents on the surface of the thin film of metal is studied. Practical recommendations regarding dimensions and the shape of indents are given. In addition, the influence of nonregularities in real metal, such as granolas inside the metal and the roughness of the surface of the metal, are studied.

Fermions in a potential energy box with an indented wall

I begin with the general case of an elementary particle in the potential energy box. Assume a potential energy box with one of the walls modified as shown on Fig. 1. Let the potential energy of the particle inside the box volume be equal to zero, and outside the box volume equal to U. There is a potential energy jump from zero to U at any point on the walls of the box. Let us assume that five walls of the potential energy box are flat and the sixth wall is modified as shown on fig.1. The indents on the sixth wall have the shape of strips having depth of a and width of b. We name the box shown on fig. 1 "modified potential energy box" (MPEB) to distinguish it from the ordinary potential energy box (OPEB) for which all walls are flat.

The behavior of a particle in the OPEB is well known. The Schroedinger equation for particle wave function inside the OPEB has form [3]:

$$d^2\psi/dx^2 + (8\pi^2 m/h^2)E\psi=0 \qquad (1)$$

Here ψ is the wave function of the particle, m is the mass of the particle, h is Planck's constant, and E is the energy of the particle. Equation (1) is written for the one dimensional case. General solution of (1) is given in the form of two flat waves moving in directions X and -X.

$$\psi(x)=A\exp(ikx)+B\exp(-ikx) \qquad (2)$$

here A and B are constants and k is the wave vector

$$k=[(2mE)^{1/2}]/(h/2\pi) \qquad (3).$$

It is well known that in the case of $U=\infty$, the solution for equation (1) is defined by the boundary condition $\psi=0$ outside the OPEB as follows:

$$\psi=C\sin(kx) \qquad (4).$$

Here C is constant. Let the width of the OPEB be L. Then the boundary conditions $\psi(0)=0$ and $\psi(L)=0$ will give the solution to Schroedinger's equation in the form of $\sin(kL)=0$ from where we get $kL=n\pi$ ($n=1, 2, 3,\ldots$). We have a well-known discrete series of possible wave vectors corresponding to possible quantum states

$$k_n=n\pi/L \qquad (5)$$

and according to (3) discrete series of possible energies $E_n=n^2(h^2/8mL^2)$.

But if the potential energy box has a modified wall, what happens to the boundary conditions for the elementary particle wave function? One more boundary condition should be added. The wave function should be equal to zero not only at x=0 and $x=L_x+a$, but also at the point $x=L_x$ (Fig.2). Yet another additional boundary condition is added because the modified wall could be divided into two parts with equal area. The first part is situated at distance L_x from the opposite wall, while the second part is situated at

distance L_x+a from the opposite wall. Once $U=\infty$ is true for every point of both parts of the modified wall, $\psi=0$ is true also for every point of both parts of the modified wall. Because of that we have $\psi(L_x)=0$ and $\psi(L_x+a)=0$. And, as shown above, $\psi=0$ for the unmodified wall, which results in a final added boundary condition $\psi(0)=0$. In total, we have the following three boundary conditions in the X direction:

$$\psi(0)=0,\ \psi(L_x)=0 \text{ and } \psi(L_x+a)=0 \qquad (6).$$

There is no general solution of (1) which will be true for any pair of L_x and a, unlike the case of OPEB in which we will have solutions for any L . To find possible solutions we begin from the last two boundary conditions in (6). It is obvious that the last two boundary conditions define possible solutions, just as they do for the OPEB of width of L=a. The wave function should be zero at points L_x and L_x+a. Possible solutions are sinusoids having a discrete number of half periods equal to a (Fig.2). The first boundary condition from (6) will be automatically satisfied together with the last two boundary conditions only in the case that

$$L_x=pa \qquad (7)$$

where p=0, 1, 2, 3, … There will be some solutions also for the case $L_x \neq pa$. For example in the case $L_x=pa/2$ we will have solutions satisfying all three boundary conditions for n=2, 4, 6,… It is obvious that number of solutions satisfying all boundary conditions (6) will be maximum in the case $L_x=pa$. Because of that let's assume $L_x=pa$, keeping in mind that we have already maximized possible solutions.
Let's assume we have MPEB which has dimensions satisfying condition (7). Then solutions will be

$$k_n=n\pi/a \qquad (8)$$

just as we had for the OPEB (5) of width L=a. However, the whole width of the box is replaced by a part of it (L_x+a is replaced by a). It is interesting to compare solutions for MPEB (8) and OPEB of width of $L=L_x+a$ (in this one dimensional case). Solutions for OPEB having width of $L=L_x+a$ will be

$$k_n=n\pi/(L_x+a) \qquad (9)$$

and the solution for the MPEB will be (8). There are fewer possible k-s in the case of the MPEB compared to an OPEB of the same width. Here we come to a very important conclusion: Modifying the wall of the potential energy box as shown in Fig.1 leads to a decrease in the number of possible quantum states. More precisely, altering the potential energy box leads to decrease in the number of possible wave vectors per unit length on k line $(L_x+a)/a$ times. This last equation is easily obtained from (8) and (9).

Until now we were working on the one dimensional case. Let's return to Fig. 1 and study the Y and Z dimensions as well. In the case of $a<<L_x, L_y, L_z$ we will have an OPEB solutions of equation (1), for Y and Z directions. Both walls for Y and Z dimension are flat and once a is small enough it will not influence the solutions of

Schroedinger equation for both Y and Z dimensions considerably. Because of that we will have: $k_x=n(\pi/a)$, $k_y=n(\pi/L_y)$, $k_z=n(\pi/L_z)$ and the volume of elementary cell in k space will be

$$V_m=\pi^3/(a\ L_y\ L_z) \qquad (10)$$

Which is again $(L_x+a)/a$ times more than the volume of the elementary cell in k space for the OPEB $V_m=\pi^3/[(L_x+ a)\ L_y\ L_z)]$. Volume in k space for three dimensional case changes like linear dimension on k line in the one dimensional case. Because of that we can easily extrapolate results we have in one dimensional case to the 3D case.

Returning back to the one dimensional case, let's conduct the following imaginary experiment: we have two potential energy boxes of the same dimensions, one an OPEB with all walls flat, and another a MPEB with one wall modified. Posit a large number of fermions. Let's put an equal number of fermions, one at a time, in both of the potential energy boxes and observe the wave vector and energy of the most recently added fermion in both boxes. The first fermion in both boxes will occupy quantum state $k_0=0$ in ordinary box and $k_{m0}=0$ in MPEB. The second fermion in OPEB will occupy $k_1=\pi/(L_x+a)$ and in MPEB $k_{m1}=\pi/a$. If we continue adding equal number of fermions to both boxes we will get $k_n=n\pi/(L_x+a)$ for the OPEB and $k_{mn}=n\pi/a$ for the MPEB. It is obvious that the n^{th} fermion will have $(L_x+a)/a$ times more wave vector in the MPEB than in the OPEB. Correspondingly, the energy of the n^{th} fermion in the MPEB will be $[(L_x+a)/a]^2$ times higher than in the OPEB. This is only true for the one dimensional case. It is not difficult to prove (it will be done in next division) that for three dimensional case, the ratio of energies of the n^{th} pair of fermions will be

$$(E_m/E)=[(L_x+a)/a]^{2/3} \qquad (11).$$

here E_m is the energy of n^{th} fermion in the MPEB and E is the energy of the n^{th} fermion in the OPEB. Index n is skipped in formula (11) because the ratio of energies does not depend on it.

Free electrons in the metal with modified wall

Free electrons inside the solid state is one of the examples of fermions inside the potential energy box. The theory of electron gas inside the lattice is well developed and is based on different models, most simple of which is the quantum model of free electrons, which gives excellent results when applied to most metals. It is well known that free electrons in metal form a Fermi gas. Boundary condition $\psi=0$ outside the metal is used in all theories because in metals the potential energy barrier is high enough to allow that simple approximation. In the quantum theory of free electrons, cyclic boundary conditions of Born-Carman

$$k_x=2\pi n/L \qquad (12)$$

are used instead of (5). Here n=0, ±1, ±2, ±3,… Cyclic boundary conditions leave the density of quantum states unchanged, and at the same time they allow us to study running

waves instead of standing waves, which is useful for Physical interpretation. The result of the theory is Fermi sphere in k space. All quantum states are occupied until k_F at T=0. k_F is maximum wave vector inside the metal at T=0 because states with $k>k_F$ are empty.

Now let's see what happens when we modify one of the walls of the metal (fig.1). As shown above, the distance between quantum states in k space in k_x direction will become $2\pi/a$ instead of $2\pi/(L_x+a)$. The number of quantum states per unit volume in k space will decrease $(L_x+a)/a$ times. Metal retains its electrical neutrality, which means that the same number of free electrons, have to occupy separate quantum states inside the metal. Because the number of quantum states per unit volume in k space is less than in the case of ordinary metal, some electrons will have to occupy quantum states with $k>k_F$. This shows that the Fermi wave vector and the corresponding Fermi energy level will increase.

We then calculate the maximum wave vector k_m at T=0 for metal with a modified wall (fig.1). Posit that the lattice is cubic, the metal is single valence, and the distance between atoms is d. The volume of metal box shown on fig.1 is

$$V=L_yL_z(L_x+a/2) \qquad (13).$$

Number of atoms inside the metal is $q=V/d^3$. The number of free electrons is equal to q and we have

$$q=L_yL_z(L_x+a/2)/d^3 \qquad (14)$$

for the number of free electrons. The volume of elementary cell in k space is

$$Ve=(2\pi/a)(2\pi/L_y)(2\pi/L_z) \qquad (15)$$

And the volume of the sphere of the radius of k_m in k space is

$$V_m=(4/3)\pi k_m^3 \qquad (16),$$

here k_m is maximum possible k in the case of modified wall and V_m is the volume of modified Fermi sphere in k space. Number of possible $\mathbf{k}=\mathbf{k_x}+\mathbf{k_y}+\mathbf{k_z}$ in k space is V_m/V_e. Each **k** contains two quantum states occupied by two electrons with spins 1/2 and –1/2. Using (14), (15), (16) we will have

$$(q/2)=(k_m^3aL_xL_z/6\pi^2) \qquad (17),$$

and for the radius of modified Fermi sphere

$$k_m=(1/d)[3\pi^2(L_x/a+1/2)]^{1/3} \qquad (18).$$

It is well known that the radius of a Fermi sphere k_F for an ordinary metal does not depends on its dimensions and is $k_F=(1/d)(3\pi^2)^{1/3}$. Comparing the last with (18) we get

$$k_m= k_F\,(L_x/a+1/2)^{1/3} \qquad (19).$$

Formula (19) shows the increase of the radius of the Fermi sphere in the case of metal with modified wall in comparison with the same metal with flat wall. If we assume $a<<L_x, L_y, L_z$ formula (19) could be rewritten in the following simple form:

$$k_m=k_F(L_x/a)^{1/3} \qquad (20).$$

According to (3) the Fermi energy in the metal with the modified wall will relate to the Fermi energy in the same metal with the flat wall as follows:

$$E_m=E_F(L_x/a)^{2/3} \qquad (21).$$

Formulas (20) and (21) are grounded in pure Mathematics. Well-known boundary conditions and well-known solutions of Schroedinger equation, combined with a very unusual geometry for the metal wall results in an increase of the Fermi level in the metal.

An obvious question emerges: let's assume that we made ratio L_x/a high enough for E_m to exceed vacuum level. What will happen? If we assume that some electrons have energies greater than the vacuum level, they will leave metal. The metal, as a result, will charge positively, and the bottom of the potential energy box will go down on the energy scale, because metal is charged now and it attracts electrons. Once the bottom of the potential energy box decreases, vacant places for electrons will appear at the top region of potential energy box. Electrons left the metal will return back because of electrostatic force and occupy the free energy states. Accordingly, E_m will not exceed the vacuum level. Instead, the bottom of the potential energy box will go down exactly at such distance to allow the potential energy box to carry all electrons needed for electrical neutrality of the metal. Regarding the work function it is clear that increasing the ratio of L_x/a will decrease first until it gets equal to zero. Even with a further increase in L_x/a, the work function will remain zero. In real metals surfaces are newer ideally flat. Roughness of the surface limits the increase of fermi level. Limits of increasing of the fermi level will be discussed in more details in next division of current article.

It is useful to recall here that analysis was made within the limits of quantum theory of free electrons. Model of free electrons give excellent results for single valence metals. As it will be shown later Gold (which is single valence) is only metal in which described structure could be practically realized. More developed theories, which take into account electron-lattice and electron-electron interaction could be used to obtain more precise results. However results obtained in this Letter will remain valid within all theories at least for the region $(-\pi/d)<k<(\pi/d)$, where d is lattice constant. Dimensional effects in semiconductor and semimetals were studied theoretically [4, 5]. Particularly influence of thin film dimensions on its Fermi level, is studied in [5].

Problems of practical realization and possible solutions

An achievable structure, which satisfies the requirements given in this Letter is shown by (fig.3). This type of structure could be obtained in the way of depositing of a thin metal film on the insulator substrate, and then etching the indents inside the metal film. What are the limitations? If we return to formulas (2) and (4) we see that flat waves

are solutions of the Schroedinger equation. A standing wave comprises two flat waves moving in the direction of X and –X. Wave diffraction will take place on the indent. Diffraction on the indents will lead to the wave "ignoring" the indent, which changes all calculations above. Consequently, results obtained are valid only when the diffraction of the wave on the indent is negligible, or

$$b >> \lambda_0 = 2a \qquad (22)$$

Here $\lambda_0 = 2\pi/k_0$ is de Broglie wavelength of electron with wave vector k_0 (n=0 on fig. 2). It is obvious that (22) will be automatically valid for n=1, 2, 3,…

Another theoretical requirement is that L_x should be multiple of a (7). In the case (7) is not valid, the number of quantum states will be less than the number given by formula (8). Decreasing the number of quantum states will magnify the effect of increasing of E_F, but it will be problematic to control work function decrease without keeping (7) valid during the metal film deposition stage, as well as during indent etching. On the other hand if (7) is deliberately kept not valid it will lead to eliminating of possible quantum states from E=0 to energy level defined by roughness of the surface (discussed later in this section).

There are some requirements to the homogeneity of the metal film. The film should be as close to mono crystal as possible. This requirement is because the wave function should be continuous on the whole length of L_x+a, which means that the metallic film could not be granular. If the metallic film is granular, the wave function will have an interruption on the border of two grains, and the indented wall's influence on the boundary conditions will be compromised. It is necessary to note here that lattice impurities do not influence free electrons with energies $E<E_F$. In order to interact with an impurity inside the lattice, the electron should exchange the energy with the impurity in the lattice. That type of energy exchange is forbidden because all quantum states nearby are already occupied. The mean free path of an electron, sitting deep in Fermi sea is formally infinite. So the material of the film can have impurities, but it should not be granular. That type of requirement is quite easy to satisfy for thin metal films.

The surface of the film should be as flat as possible, as surface roughness leads to the scattering of de Broglie waves. Scattering is considerable for the wavelengths of the order or less than the roughness of the surface. Substrates with a roughness of 5 A are commercially available. Metal film deposited on such substrate can also have a surface with the same roughness. The de Broglie wavelength of a free electron in metal sitting on the Fermi level is approximately 10 A^0. Scattering of the de Broglie wave of electrons having energies $E>E_F$ will be considerable. Consequently, energy states with energies $E>E_F$ will be smoothed. Smoothing of energy levels decrease the lifetime of the energy state and lead to continuous energy spectrum instead of discrete one. Fig. 4 shows comparison of fermi and vacuum levels of some single valence metals on the energy scale and simultaneously on the scale of de Broglie wavelength of the electron calculated from formula (3). It is evident that 5 A roughness of the surface is enough to eliminate energy barrier (in the case $L_x \neq pa$) for such metals as Cs and Na. The same roughness creates gap from zero to approximately fermi level in energy spectrum of such metals as Au and Ag.

It is evident that the depth of the indent should be much more than the surface roughness. Consequently, the minimum possible a is 30-50 A. According to (22) the minimum possible b will be 300-500 A. These dimensions are well within the capabilities of e-beam lithography and ion beam milling. The primary experimental limitation in the case of the structure shown on fig.4 is that the ratio $(L_x/a) \geq 5$, in order to achieve a work function which is close to zero. Consequently, the thickness of the metal film should be at least 180-300 A^0. Usually films of such thickness still repeat the substrate surface shape, and the film surface roughness does not exceed the roughness of the base substrate. However, the same is not true for metal films with a thickness of 1000 A^0 and more, because a thick film surface does not follow the surface of the substrate. That puts another limit $15 \geq (L_x/a) \geq 5$ on the dimensions of the structure, when metal films are deposited on the substrates. Other possible solutions, such as metal crystals of macroscopic dimensions like those frequently used for electron beam microscope cathodes, will not be limited by the same requirements.

And finally there are some limits on materials which could be used for thin film. Most metals oxidize under influence of atmosphere. Even when placed in vacuum metals oxidize with time because of influence of residual gases. Typical oxides have depth of 50-100 A which is considerable on the scale I discussed. Because of that Gold is only material which could be used in practice.

Conclusions

It has been shown that modifying the wall of a potential energy box changes the boundary conditions for the wave function of an elementary particle inside the potential energy box. New boundary conditions decrease the number of solutions to Schroedinger's equation for a particle inside the MPEB. If the particles are fermions, the decrease in the number of quantum states results in an increase in the energy of the n^{th} particle situated in the potential energy box. General results obtained for fermions in the potential energy box were extrapolated to the particular case of free electrons inside the metal. Calculations were made within the limit of quantum theory of free electrons. It was shown that in the case of a certain geometry of the metal wall, the Fermi level inside the metal will increase. A controllable increase in the Fermi level, and the corresponding decrease of the work function of the metal will have practical use for devices working on the basis of electron motion, electron emission, electron tunneling etc. A discussion of the practical possibilities to realize the modified wall in a metal shows that electron beam lithography and ion beam milling are capable of practical realization.

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Figure captions

Fig.1 Three dimensional potential energy box with indented wall. a is the depth of the indent and b is width of the indent. Potential energy is zero everywhere inside the box volume and is infinity everywhere outside of box volume. Maximum dimension in X direction is L_x+a.

Fig.2 Potential energy box together with solutions of Schroedinger equation. Boundary conditions $\psi(L_x)=0$ and $\psi(L_x+a)=0$ define solutions of Schreginger equations as shown on the right side of the figure.

Fig.3 Possible realization of metal with indented wall. Indents are etched on the surface of thin metal film deposited on insulating substrate.

Fig. 4 Energy diagrams of some single valence metals on the scale of de Broglie wavelength calculated as $\lambda=2\pi/k$ from (3).

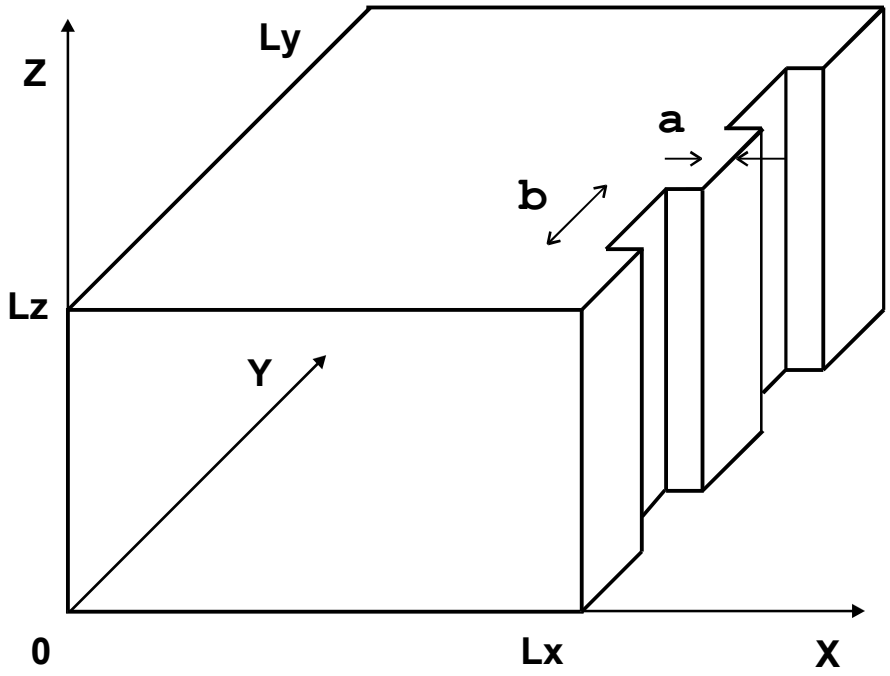

Fig. 1

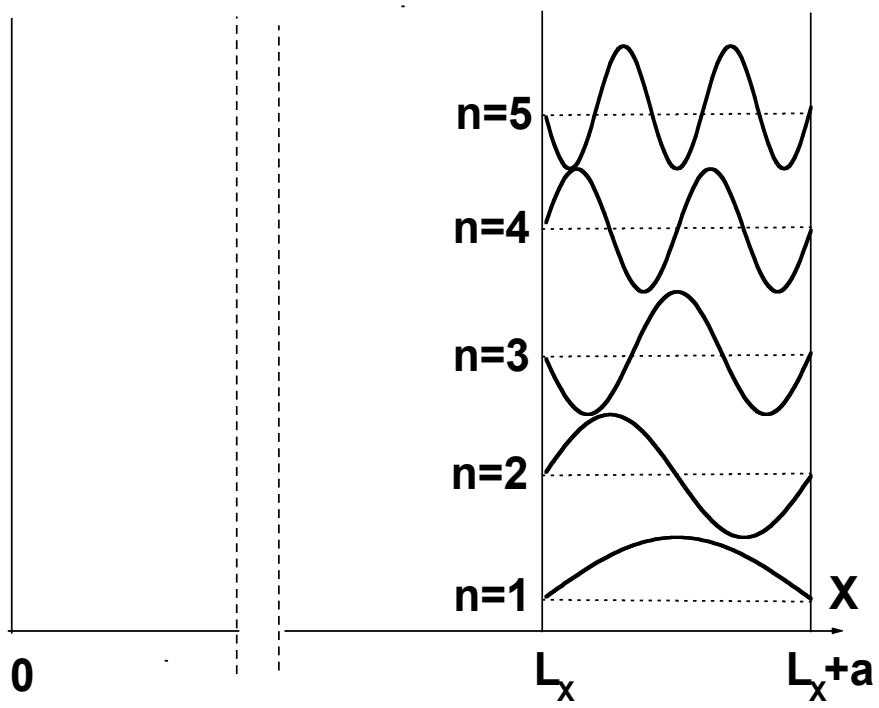

Fig.2

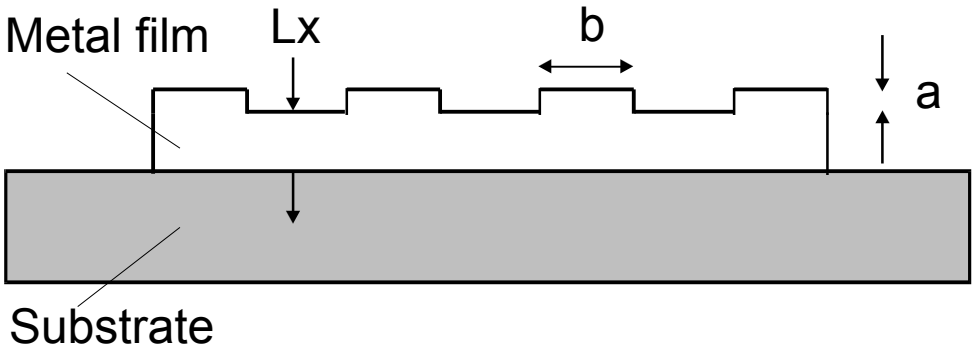

Fig. 3

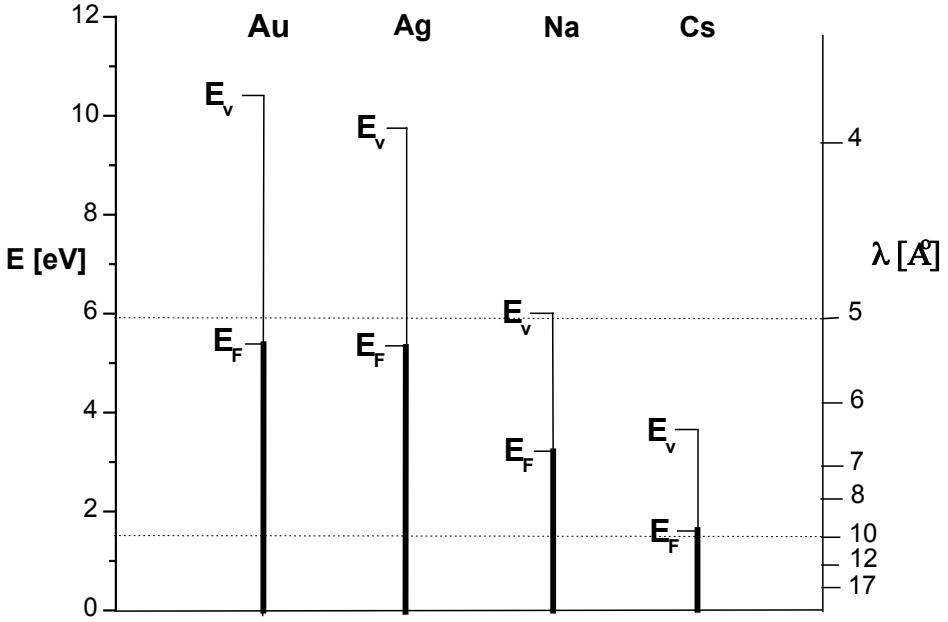

Fig. 4