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LASER INDUCED ELECTRODEPOSITION ON
POLYIMIDE AND GaAs SUBSTRATES

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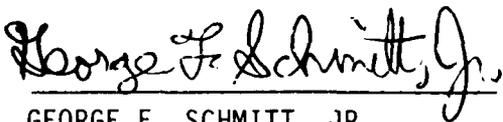
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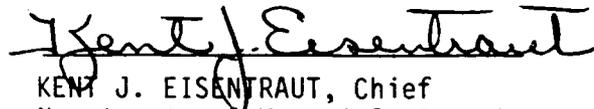
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SUMMARY

The work described in this report has been conducted together with G.F. Schmitt and M. Halliwell at the Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433-6533 during the period of April 17, 1983 to April 29, 1983.

Electrodeposition of gold and palladium-nickel on semiconductor GaAs and polyimide polymer substrates was carried out making use of a switched YAG-Nd laser without external electric current.

Deposits were characterized by SEM, x-ray analysis and their resistance on GaAs substrate were correlated with laser energy density used.

1. INTRODUCTION

1.1 Objectives

The main goals of the work described in this report were:

- a. Exploring the feasibility of laser induced direct metal electroplating on semiconductor GaAs and polymer polyimide substrates.
- b. Better understanding and characterization of the relationship between mode of laser operation and deposit morphology, structure and properties.

1.2 Significance

Establishing high rate highly selective electroplating process making use of laser beam without masking and external electrical current.

Obtaining ohmic or Schottky barrier contacts through direct laser induced plating on semiconductor substrates.

Obtaining direct deposit by laser induced electroplating on polymeric substrate compared to conventional electroless processes.

2. EXPERIMENTAL AND PROCEDURE

2.1 Experimental Set Up

Schematic outline of the experimental system is shown in Fig. 1. The system consisted of laser beam facilities, x-ray computerized table, electrolytic cell and computer.

2.1.1 Laser System

The laser system used in this work was a Q-switched laser Nd: YAG made by Quantel Company. Laser beam diameter ranged from 0.5mm to 25mm, pulse duration was $15 \cdot 10^{-9}$ sec and repetition rate of 1.0 Hz.

2.1.2 Operation Conditions

Laser energy density upon the irradiated substrate samples could be controlled and changed by inserting absorbing filters between the laser beam source and the optical lens. These filters, produced by Pyrex Corning Company, consisted of various types as described in Table 1. Laser energy density ranged from 0.1 to 2.0 joule/cm².

Experimental Set-Up

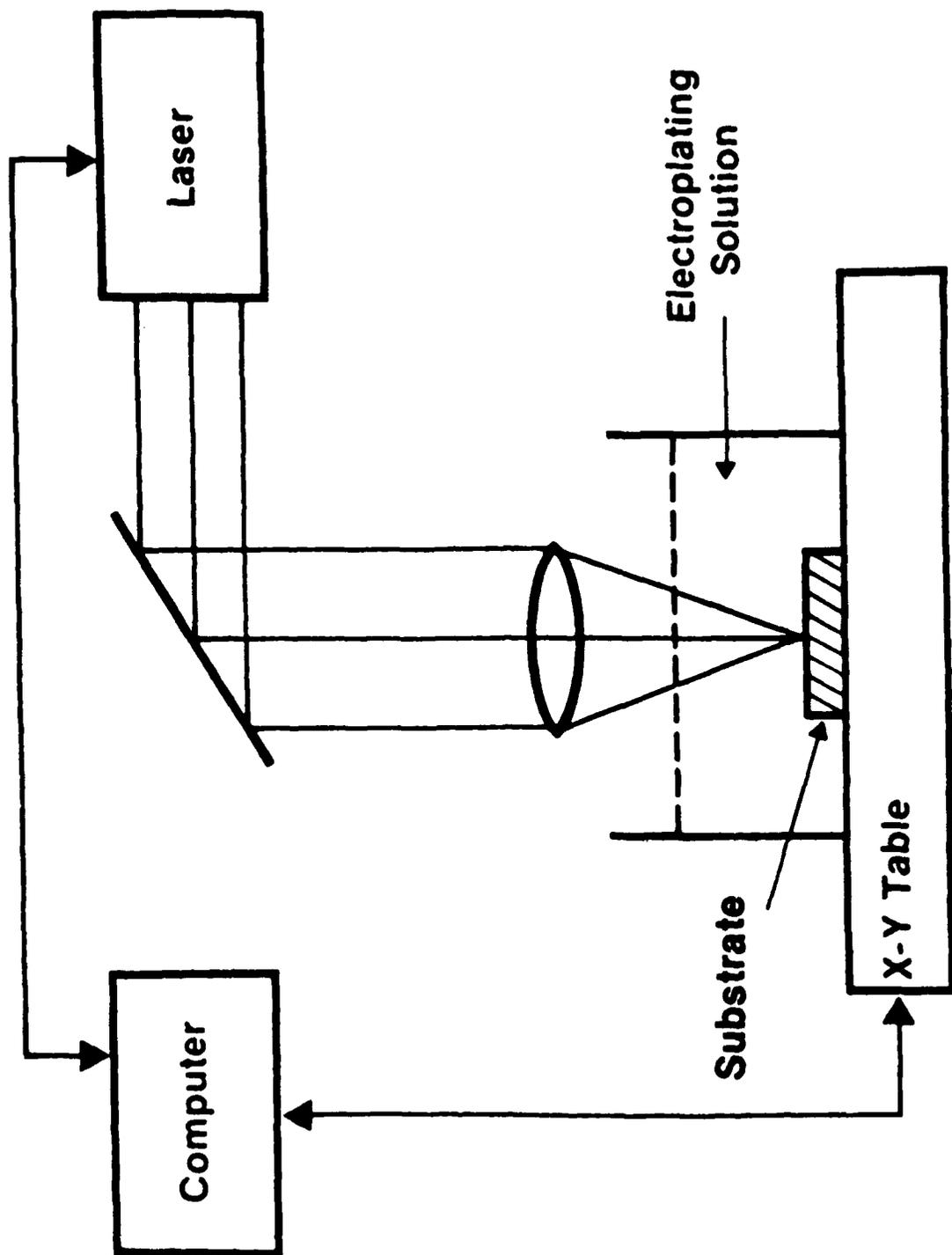


FIGURE 1.

TABLE 1: TYPE OF ABSORBING FILTERS

<u>Filter No.</u>	<u>Designation Code</u>	<u>Thickness (mm)</u>	<u>Code No.</u>
1	CS0-54	2.0	# 0160
2	CS3-74	1.59	# 3391
3	CS3-72	2.96	# 3387
4	CS2-58	2.45	# 2403
5	CS2-64	4.43	# 2030

2.2 Materials

2.2.1 Substrate Materials

2.2.1.1 Semiconductors

Undoped GaAs (100) specimens were prepared to give flat squares of 15 x 15 mm.

2.2.1.2 Polymers

Specimen 20 x 30 mm in size were prepared from polyimide sheet produced by Dupont Company and known as Kapton H-500.

2.2.2 Electrolytic Plating Solution

2.2.2.1 Gold Plating

Potassium-Gold-Cyanide solution. (Lea-Ronal Co. Auropred CVD Solution)

2.2.2.2 Nickel-Palladium

Nickel-Palladium plating solution. (Lea Ronal Co. Pallamet 75 Solution)

These solutions were commercial electroplating solutions for use in various electronic and microelectronic devices.

2.3 Laser Induced Plating Procedure

Specimens were immersed in plating solution where the liquid over the substrate was about 1 mm. The solution was kept at room temperature and no external power supply was used. Thereafter specimen surfaces were laser irradiated under various conditions and at various locations according to desired preplanned program making use of the computer as shown schematically in Fig. 1

2.4 Deposit Observation

Deposits obtained through laser irradiation on immersed substrate in electroplating solution were examined and characterized by several methods.

2.4.1 Microscopy

Optical, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) are very effective techniques in characterizing deposit morphology, structure and composition.

2.4.2 Surface Analysis

Auger Spectroscopy and Electron Spectroscopy for Chemical Analysis (ESCA) are very powerful techniques in analyzing elements and compounds of surface electrodeposition coatings especially thin coatings such as those obtained in this work by laser induced plating.

2.4.3 Electrical Measurements

Electrical properties of the electrodeposits obtained on semiconductor substrate were characterized by measuring their resistance. Measurements were carried out with two Tungsten probes 0.5 mm in diameter. Potential current curves were detected by Tetronix Model 576 curve tracer. The distance between the two probes while measuring was one millimeter.

3. RESULTS AND DISCUSSIONS

High speed, highly selective laser induced gold, Palladium-Nickel electroplating without masking and external electric current on GaAs semiconductor substrate and on polyimide polymeric substrate were achieved in this work.

3.1 Laser Gold Plating on Undoped GaAs (100) Substrate

3.1.1 Deposit Formation

Gold deposition on GaAs substrate was obtained under various laser conditions as shown in Tables 1, 2 and 3. Deposits were formed using laser energy densities in the range of 0.3 joule/cm² to 2.0 joule/cm² (Tables 1 and 2) and 0.15 joule/cm² to 0.30 joule/cm² (Table 3.3).

Laser pulse duration was 15 ns while pulse overlap was 50% (Tables 1 and 2) and 95% (Table 3) with beam diameter of 0.6 mm to 0.7 mm.

TABLE 2 Undoped GaAs (100) SAMPLE I, SIDE 1						
GOLD PLATING SOLUTION (Lea-Ronal Co. Aurospeed CVD Solution)						
Exp. No.	Laser Energy Density (joule/cm ²)	Absorption Filter Used (percents)	No. of Pulses	Pulse Overlapped (%)	Laser Beam Diameter (mm)	Pulse Duration (ns)
1	2.0	---	1	50	0.6	15
2	1.0	---	1	50	0.6	15
3	0.5	50%	1	50	0.6	15
4	1.0	---	1	50	0.6	15
5	0.8	20%	1	50	0.6	15
6	0.3	70%	1	50	0.6	15

TABLE 3 Undoped GaAs (100) SAMPLE I, SIDE 2						
GOLD PLATING SOLUTION (Lea-Ronal Co. Aurospeed CVD Solution)						
Exp. No.	Laser Energy Density (Joule/cm ²)	Absorption Filter Used (percents)	No. of Pulses	Pulse Overlapped (%)	Laser Beam Diameter (mm)	Pulse Duration (ns)
1	0.3	70%	1	50	0.6	15
2	0.8	20%	1	50	0.6	15
3	0.5	50%	1	50	0.6	15
4	1.0	---	1	50	0.6	15

TABLE 4 Undoped GaAs (100) SAMPLE II

**GOLD PLATING SOLUTION
(Lea-Ronal Co. Aurospeed CVD Solution)**

Exp. No.	Line* No.	Laser Energy Density (joule/cm ²)	Absorption Filter Used (percents)	No. of Pulses	Pulse Overlapped (%)	Laser Beam Diameter (mm)	Pulse Duration (ns)
10	1	0.308	#4	1	95%	0.6	15
	2	to	70%				
	3	0.315					
11	4	0.249	#2 + #4	1	95%	0.6	15
	5	to 0.253					
12	6	0.164	#4 + #5	1	95%	0.6	15
	7	to 0.168					

* All line numbers represent three overlapping rows (95% overlap).

3.1.2 Deposit Morphology and Composition

Gold deposit on GaAs substrate was examined by Scanning Electron Microscope (SEM). Typical results are shown in Fig 3.1. It was found that laser induced gold deposition resulted in uniform continuous and well defined plated areas (lines) of gold as shown in Fig. 3.1. Furthermore it was found that laser induced gold plating resulted in gold deposition without substantial damage to the GaAs substrate when laser energy density up to 0.3 joule/cm² was used. (Fig. 3.1) The presence of gold in the plated zones including in the light and dark local areas was found and confirmed by x-ray image intensity pictures as shown in the middle of Fig. 3.1 (Fig. 3.1.C and Fig. 3.1.D)

LASER GOLD PLATING
 UNDOPED GaAs (100)

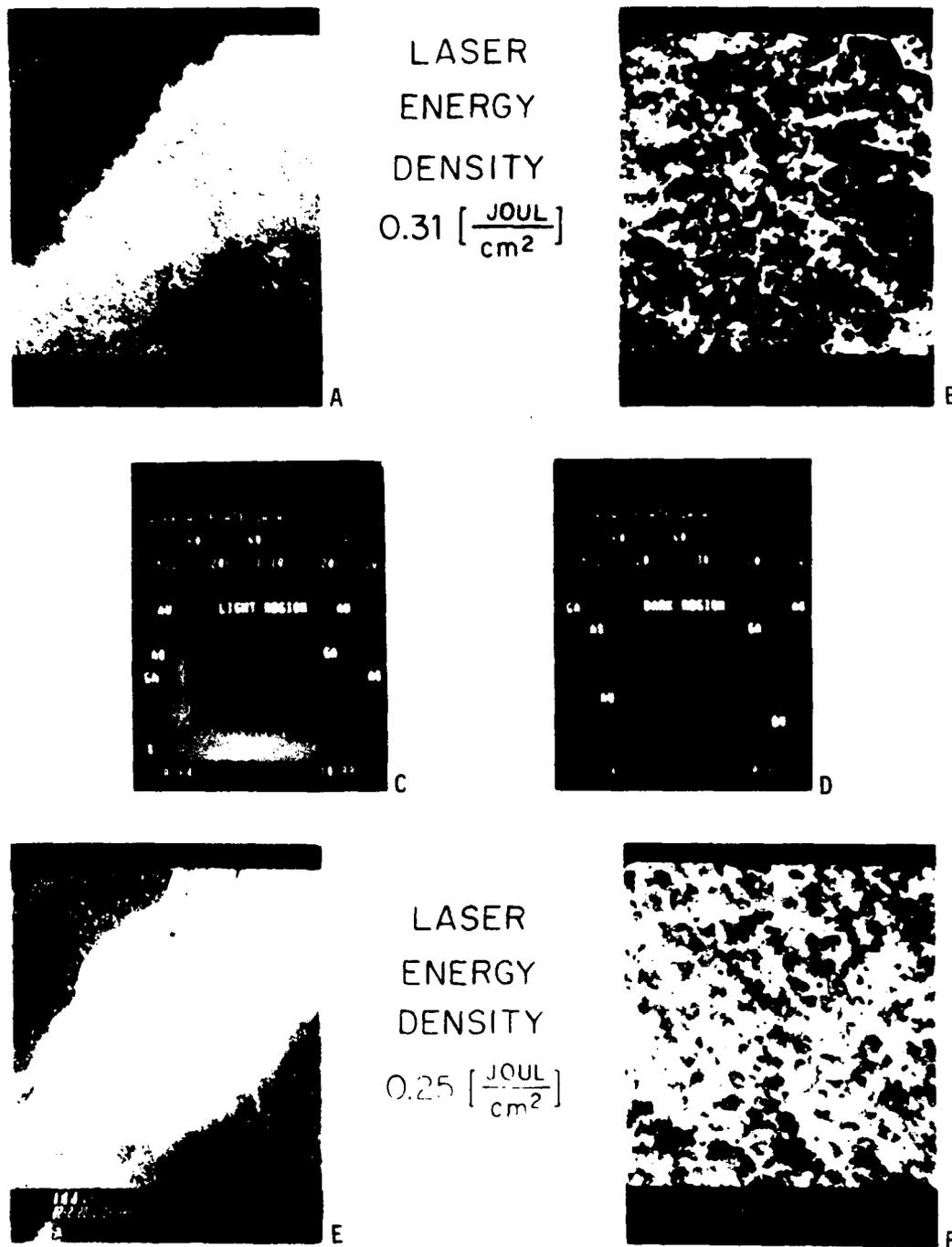


FIG. 4 Laser Gold Plating on GaAs.
 A. Gold Deposit, Laser Energy 0.31 joule/cm^2
 B. High Magnification of (A).
 C. X-ray image intensity of Gold from the Light regions in (B).
 D. X-ray image intensity of Gold from the Dark regions in (B).
 E. Gold deposit, Laser energy 0.25 joule/cm^2 .
 F. High Magnification of (E).

LASER GOLD PLATING
 UNDOPED GaAs (100)
 DEPOSIT RESISTANCE MEASUREMENT

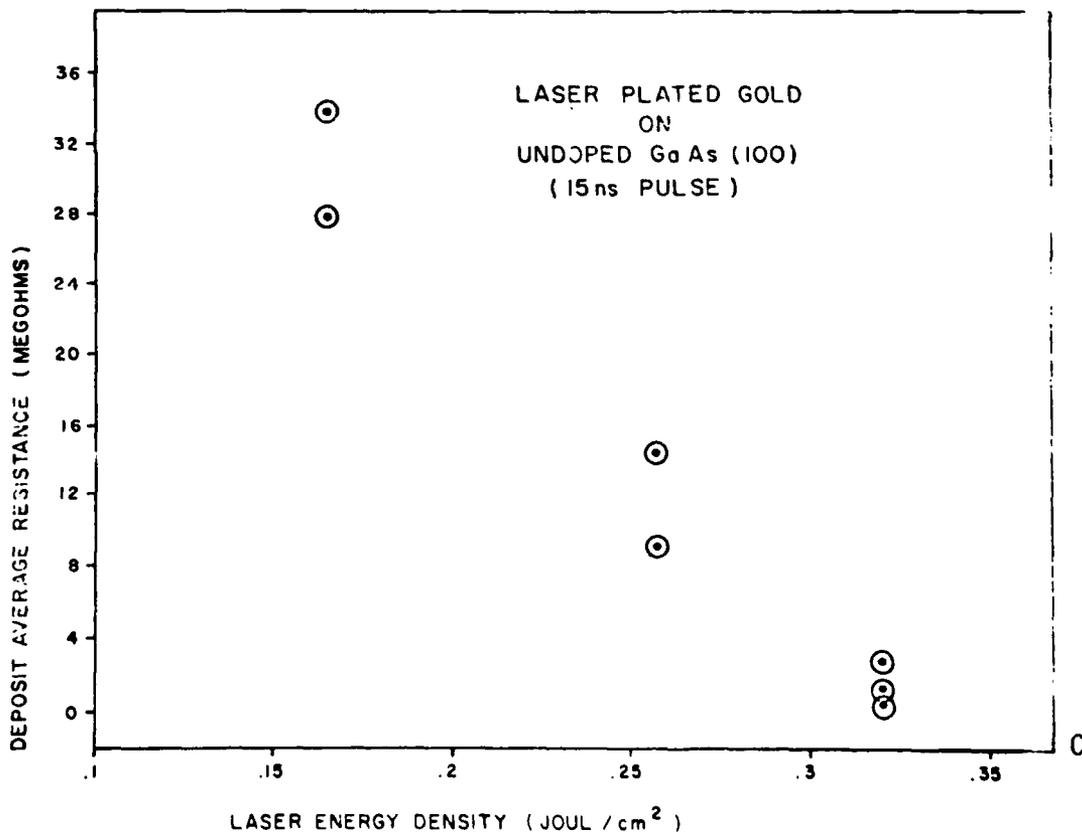
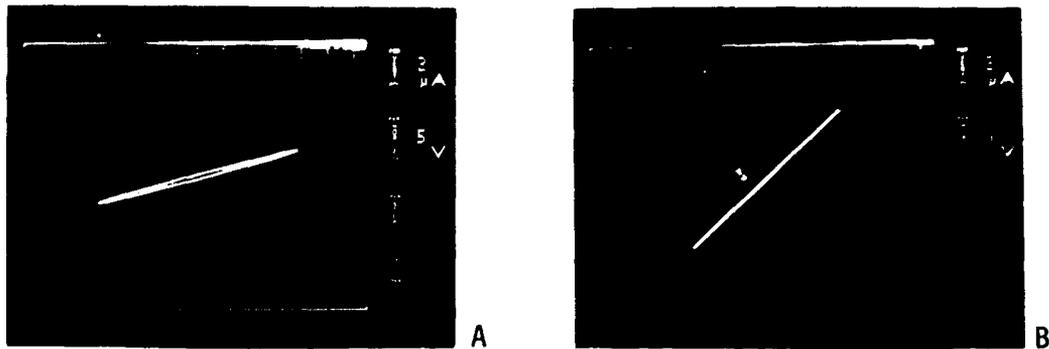


FIG. 2 Gold Deposit Resistance
 A, B. Typical current-voltage measurements.
 C. Deposit resistance as function of laser energy density used in deposit formation.

3.1.3 Deposit Electrical Resistance

The resistance of laser induced gold plating lines (Figure 4) was measured as function of laser energy density used and the results are shown in Fig. 2

Typical relationship of current - voltage is shown in Fig. 2. The calculated slopes of these I-V curves gave the electrical resistance of the deposited lines. It was found that deposit electrical resistance decreased with increase in laser energy density (Fig. 2). Minimum electrical resistance was obtained at laser energy around 0.31 joule/cm^2 where maximum gold thickness was probably formed without substantial damage to the GaAs substrate (Fig. 4).

3.2 Laser Gold Plating On Polyimide (KAPTON) Substrate

High speed, highly selective, laser induced metal or metal alloy electrodeposition on polymeric substrate without the use of masking and electrical external current or electroless solution was performed in this work. Laser induced gold plating on polyimide substrate will be described herein.

3.2.1 Deposit Formation

The feasibility of obtaining laser assisted electrodeposition of gold from electroplating solution on polyimide substrate was examined under a wide range of laser beam operational conditions as summarized in Table 5. Laser energy density ranged from 0.2 joule/cm^2 to 2.2 joule/cm^2 ; beam diameter was 0.5 mm, 0.6 mm and 1.5 mm. The number of pulses irradiated at one location was 1 and 5, pulse overlap was 50% and 95% and pulse duration was kept constant at 15 ns. (Table 5) It might be noted that laser energy density was controlled with absorption filters (Table 5, Exp. 1-4) as well as with changing the laser power source (Table 5, Exp. 5). Metallic gold deposit was observed on the irradiated zones of the polyimide substrate under all the conditions examined (Table 5).

3.2.2 Deposit Morphology and Composition

Typical view of gold laser deposition on polyimide substrate is shown in Fig. 3. Two gold deposit lines obtained directly by using laser energy density of 0.32 and 0.92 joule/cm^2 (Table 5, Exp. 5, lines 1*, 2*) are shown in Fig. 3.A. High magnification of part of the right deposit line is shown in Fig. 3.B. It was found that the bright regions were highly concentrated with gold deposit as demonstrated in Fig. 3.C. The grey or dark regions between the bright ones contained high concentration of potassium as shown in Fig. 3.D.

Furthermore, Fig. 3 showed that direct laser gold plating could be achieved without introducing direct damage to the polyimide substrate. The laser beam diameter used in obtaining the gold deposit lines (Fig. 3.A, 3.B) was 1.5 mm. Laser energy density in beam cross section was not very uniform which resulted in non-uniform gold deposit lines (Fig. 3.A, B).

However upon choosing appropriate laser beam operational conditions (Table 5, Exp. 6) it was possible to obtain uniform continuous gold deposit lines as observed in optical microscopy (Fig. 5). These gold deposit lines were obtained with laser energy densities up to 0.586 joule/cm^2 , beam diameter of 0.5 mm, pulse duration of 15 ns and pulse overlap of 95% with 5 pulses irradiation at one place (Table 5, Exp. 6).

Furthermore, it was possible to measure the electrical resistance of gold deposit lines (Exp. 6, lines 0, 1, 2) since the lines were uniform and continuous. Their electrical resistance was found to be 0.5×10^6 ohms. It should be noted that the gold lines were embedded into the polyimide substrate which probably caused their high resistance

Auger Electron Spectroscopy (AES) techniques were used to analyze the deposit with regard to the presence and distribution of gold and potassium. AES depth profile of gold deposit lines are shown in Fig. 6. The presence and distribution of gold (Au) and potassium (K) with deposit thickness is shown in Fig. 6.A. It was found that gold atomic concentration was about 20% through deposit thickness which exceeded one micron (Fig. 6.B). The presence and distribution of potassium (K), carbon (C) and Oxygen (O) are shown as well in Fig. 6.B. Potassium atomic concentration was found to be in the range of 40% to 50% through deposit thickness.

The presence of gold and potassium was also found by Electron Spectroscopy for Chemical Analysis (ESCA) examination of deposit lines (Fig. 7). Fig. 7.B shows the binding energy profile corresponding to elemental gold (Au). In other words the presence of pure metallic gold deposited on the polyimide substrate was found. Fig. 7.A shows the presence of potassium not in its elemental state but as a cation in a potassium salt such as KCl.

TABLE 5 Substrate: POLYIMIDE (Dupont Co. KAPTON, H-500)

GOLD PLATING SOLUTION
(Lea-Ronal Co. Aurospeed CVD Solution)

Exp. No.	Line No.	Laser Energy Density (joule/cm ²)	Absorption Filter Used (percents)	No. of Pulses	Pulse Overlapped (%)	Laser Beam Diameter (mm)	Pulse Duration (ns)
1	1	1	---	1	95%	0.7	15
	2	1	---	5	50%		
2	3	0.8	#2	1	95%	0.7	15
	4	0.8	80%	5	50%		
3	5	0.5	50%	1	95%	0.7	15
	6	0.5		5	50%		
4	7	0.2	#4	1	95%	0.7	15
	8	0.2	80%	5	50%		
5 (Sample #5)	1*	0.32	---	1	50%	1.5	15
	2*	0.92	---	1	50%		
	3*	1.59	---	1	50%		
	4*	2.11	---	1	50%		
	5	2.11	---	1	50%		
	6	1.56	---	1	50%		
	7	0.92	---	1	50%		
	8	0.27	---	1	50%		

* Electrolytic cell was covered by transmitted plastic cover.

TABLE 5 Continued Substrate: POLYIMIDE (DuPont Co. KAPTON, H-500)

GOLD PLATING SOLUTION

(Lea-Ronal Co. Aurospeed CVD Solution)

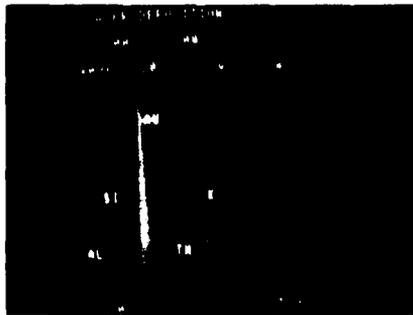
Exp. No.	Line No.	Laser Energy Density (joule/cm ²)	Absorption Filter Used (percents)	No. of Pulses	Pulse Overlapped (%)	Laser Beam Diameter (mm)	Pulse Duration (ns)
6	0	0.586	---	5	95%	0.5	15
	1		---	5	95%	0.5	15
	2		---	5	95%	0.5	15
	3	0.50	#2	5	95%	0.5	15
	4		20%	5	95%	0.5	15
	5	0.076	#3	5	95%	0.5	15
	6		85%	5	95%	0.5	15
	7	0.32	#1, #2 before half wave plate.	5	95%	0.5	15
	8		#3 before sample	5	95%	0.5	15



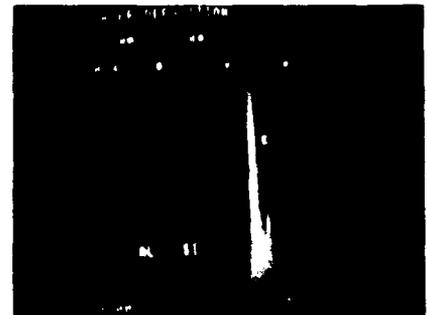
A



B



C



D

FIG. 3 Laser Gold Plating on Polyimide. SEM OBSERVATIONS
A. Gold deposit lines.
B. Magnification of the lines shown in (A).
C. X-ray intensity image of bright white areas in (B).
D. X-ray intensity image of grey areas in (B).

LASER GOLD PLATING
POLYIMID [KAPTON]

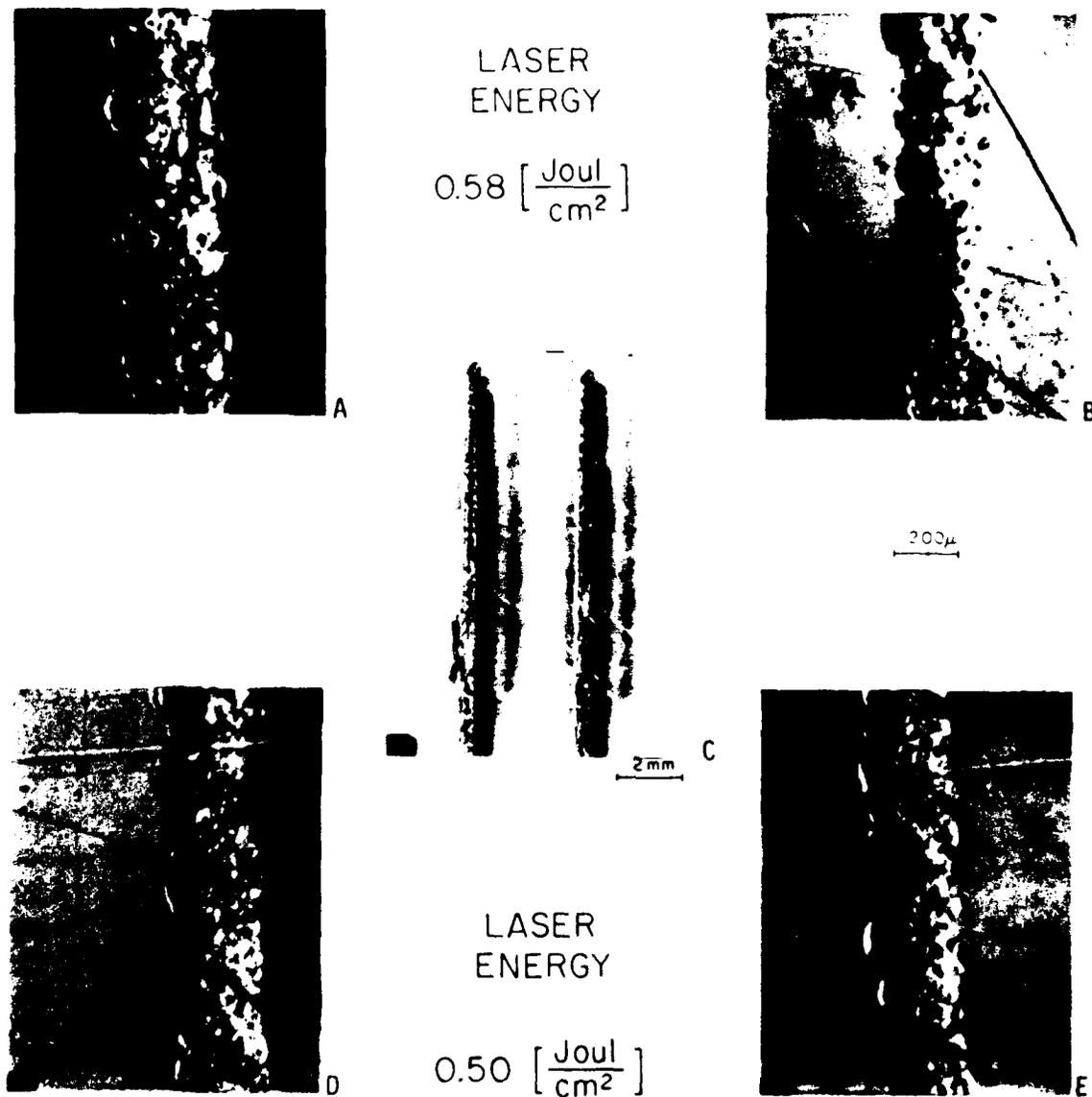


FIG. 5 Laser Gold Plating on Polyimide. Optical microscopy.
A, B. Typical Gold line deposits at laser energy of 0.58
joule/cm².
C. Low Magnification of the lines (A) and (B).
D, E. Typical Gold line deposits at laser energy of 0.50
joule/cm².

POLYIMIDE (KAPTON) SUBSTRATE AES DEPTH PROFILE OBSERVATIONS

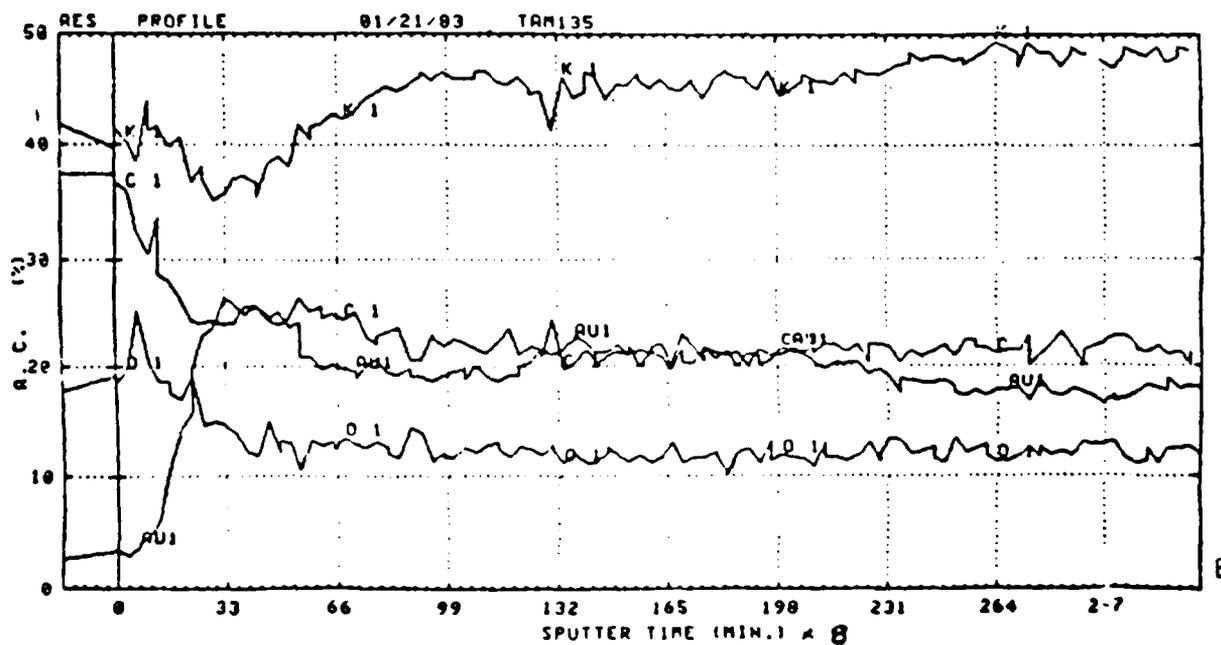
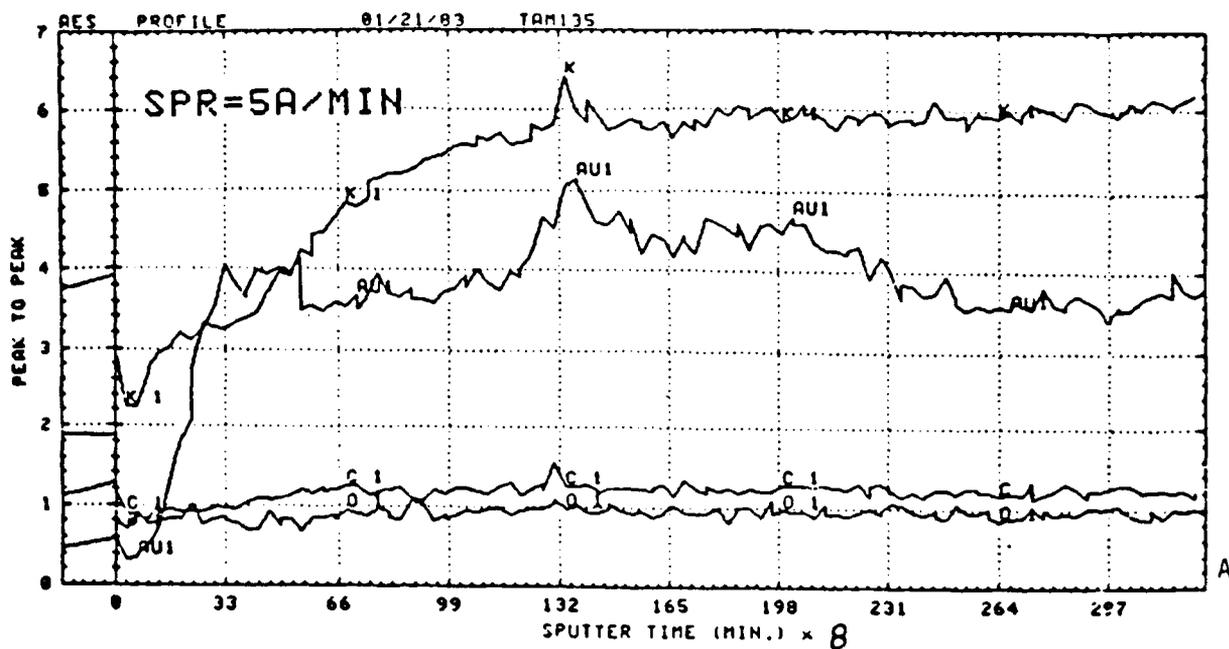


FIGURE 6.

POLYIMIDE (KAPTON) SUBSTRATE ESCA OBSERVATIONS

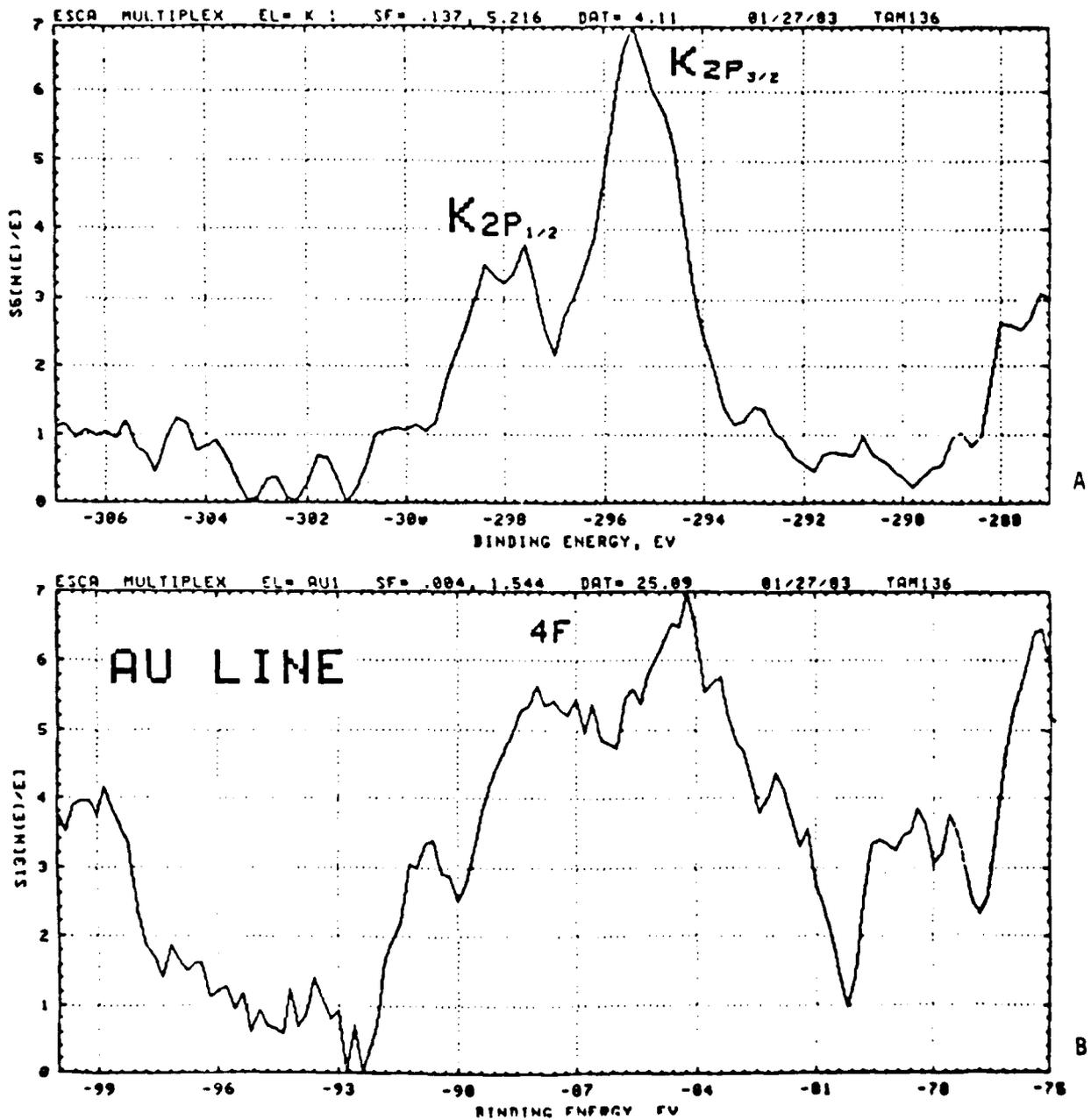


FIGURE 7.

3.3 Laser Palladium-Nickel Plating on Polyimide (KAPTON) Substrate

Laser Induced alloy plating of Palladium-Nickel on polyimide polymeric substrate was shown to be feasible in this work. Deposit formation conditions and deposit morphology and composition are described herein.

3.3.1 Deposit Formation

Selective high rate laser Palladium-Nickel plating on polyimide substrate without masking and without external current was conducted in this work. (Table 7) summarizes the various laser conditions used in producing palladium-nickel deposits on the polyimide substrate. Laser energy density ranged from 0.2 joule/cm² to 2.2 joule/cm²; laser beam diameter was 0.6 mm and 1.5 mm, while laser pulse duration was kept constant at 15 ns.

Laser irradiation consisted of 1 and 5 pulses at the same area while pulse overlap was 50% and 95% (Table 7).

Pd-Ni deposit lines were obtained on the polyimide substrate. Typical views of these deposits will be described herein.

3.3.2 Deposit Morphology and Composition

Fig. 8. shows typical SEM views of Pd-Ni deposit obtained in this work (Table 7 , Exp. 9, Lines 1* & 2*). Laser beam diameter used to obtain the deposit lines in Fig. 8 A was 1.5 mm. In such beam cross section the energy density was not uniform which resulted in non-uniform deposit lines (Fig. 8 .A, 8 .B). It might be noted that the deposit shown in Fig. 8 .B was obtained after irradiation of 5 laser pulses at the same spot. (Table 7 , Exp. 9, line 1*). The presence of Pd and Ni in the deposit was found and detected by x-ray intensity image shown in Fig. 8 .C. Besides the presence of Pd and Ni residues of chlorides, Si and Al were found (Fig. 8 .C). However, these should be regarded as impurities introduced through specimen preparation for SEM examination.

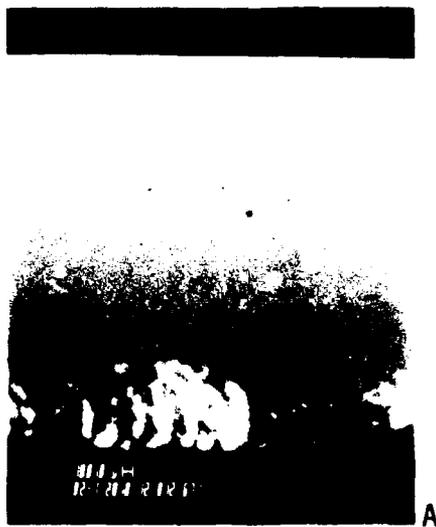
TABLE 7 Substrate: POLYIMIDE (Dupont Co. KAPTON, H-500)

PALLADIUM-NICKEL PLATING SOLUTION

(Lea-Ronal Co. Pallamet 75 Solution)

Exp No.	Line No.	Laser Energy Density (joule/cm ²)	Absorption Filter Used (percents)	No. of Pulses	Pulse Overlapped (%)	Laser Beam Diameter (mm)	Pulse Duration (ns)
5	1	0.2	#4 80%	1	95%	0.6	15
	2	0.2		5	50%		
6	3	0.5	#3 50%	1	95%	0.6	15
	4	0.5		5	50%		
7	5	0.8	#2 20%	1	95%	0.6	15
	6	0.8		5	50%		
8	7	1.0	---	1	95%	0.6	15
	8	1.0	---	5	50%		
9 (Sample #6)	1*	0.27	---	1	50%	1.5	15
	2*	0.82	---	1	50%		
	3*	1.46	---	1	50%		
	4*	2.06	---	1	50%		
	5	0.27	---	1	50%		
	6	0.97	---	1	50%		
	7	1.56	---	1	50%		
	8	2.11	---	1	50%		

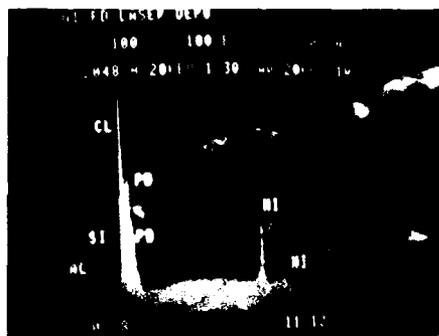
* Electrolytic cell was covered by transmitted plastic cover.



A



B



C

FIG. 8 Laser Palladium-Nickel Plating on Polyimide Substrate.

- A. Typical Deposit Lines.
- B. Magnification of the Area Shown in (A)
- C. X-ray Image Intensity for Ni, Pd obtained from the area shown in (B).

4. CONCLUDING REMARKS

A. Direct Laser induced plating of metals (i.e. Gold) and alloys (i.e. Palladium-Nickel) without external power supply on semiconductor substrate (i.e. GaAs) and polymeric substrate (i.e. polyimide) was performed and evaluated in this work.

B. It is proposed that, upon the interaction of laser pulses with semiconductor material substrate, free electrons are generated through photon absorption processes generating electron-hole pair. (9, 11, 12) In the case of polymeric substrate free radicals and free electrons are produced. The life time of these free electrons are in the range of nanoseconds (Laser pulse duration time). Therefore they could be consumed by cations present in various types of electrolyte solutions. These cations therefore become atoms deposited upon the substrate surface, and the deposit is formed.

C. Further deposit characterization should be carried on, especially in obtaining a relationship between laser operating conditions, type of electrolyte solution and type of substrate.

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